

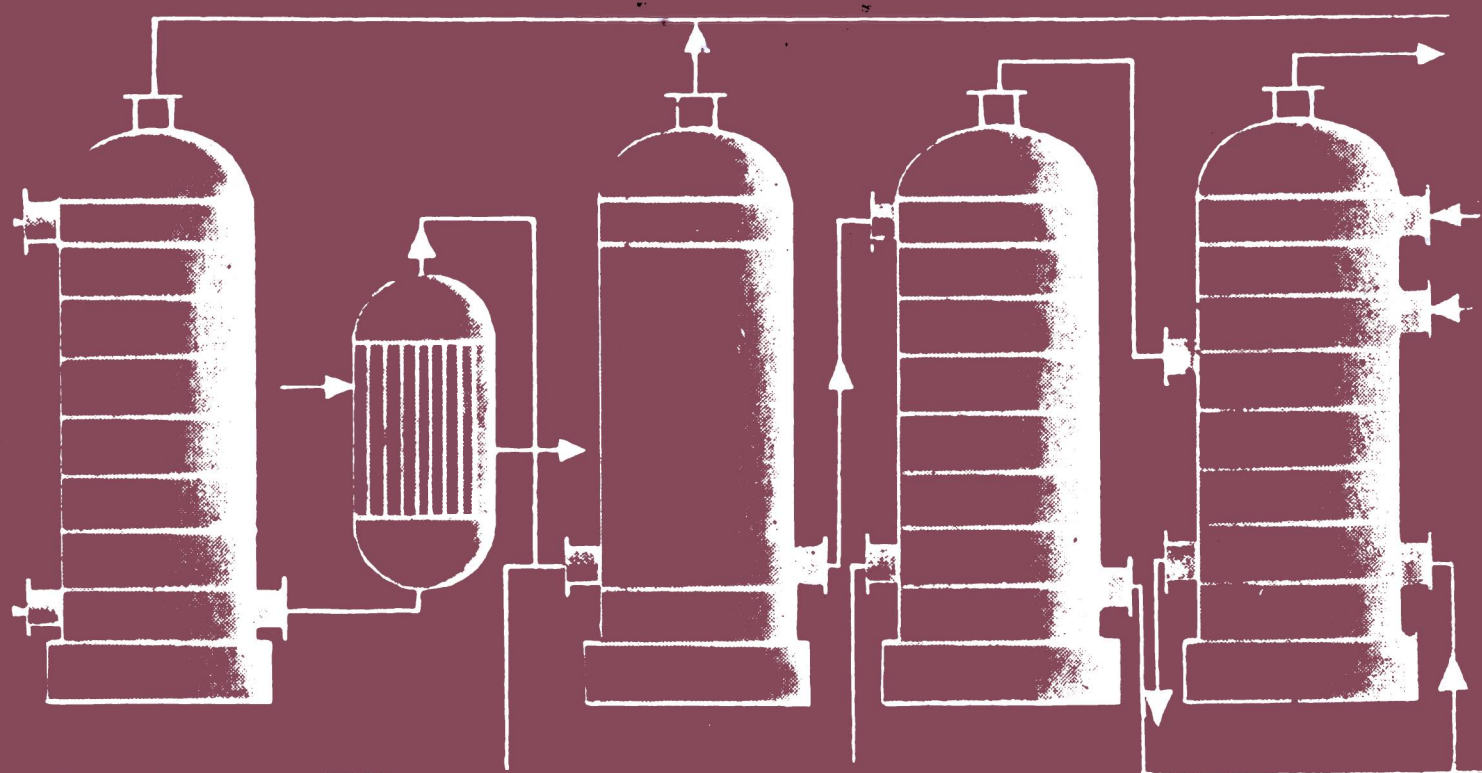
# Chemical Technology 2

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Edited  
by

I. P. Mukhlyonov, D.Sc.

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Mir Publishers



# **Chemical Technology**

**IN TWO PARTS**

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**EDITED  
BY I. P. MUKHLYONOV, D.SC.**

# The Most Important Industrial Chemical Processes

## PART 2

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# ОБЩАЯ ХИМИЧЕСКАЯ ТЕХНОЛОГИЯ

## ЧАСТЬ 2

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## Preface

There are at present more than 50 000 known inorganic chemical compounds and about three million organic ones\*. Although only a relatively small part of them are produced commercially the number of chemical products manufactured is still tremendous. The chemical industry, in the narrow sense, encompasses the manufacture of inorganic acids, alkalis, salts and oxides, products of organic synthesis, high-molecular compounds (synthetic resins, plastics, chemical fibres, rubber, varnishes, and glues)—more than 50 000 various products. Chemical technology also embraces the manufacture of building materials, metallurgy, pulp-and-paper, petroleum-refining and coal-carbonization industries, and chemical processing of shale, peat, wood, and other naturally-occurring organic materials. Tens of thousands of other products are made in these branches of industry.

It is, of course, impossible to describe all these manufacturing processes in a textbook on chemical technology. Therefore, the textbook is devoted only to typical chemical engineering processes and the equipment in which they are carried out, using as examples those branches of the chemical industry which are of the most importance.

A distinction is made between the technology of organic products and the technology of inorganic products. However the border line between them is not very definite since both organic and inorganic compounds are used jointly as raw materials in many industrial processes, and reactions between organic components yield both organic and inorganic products. There are industrial processes in which organic compounds are produced from inorganic substances, for example the manufacture of urea from ammonia and carbon dioxide. The processes of manufacturing organic and inorganic products are often interrelated and can rationally be combined at one and the same chemical factory. Thus, for carrying out hydrogenation, chlorination, hydrochlorination, nitration, sulfonation and saponification of organic compounds corresponding inorganic substances are employed and they are manufactured at the same factory as the organic compounds.

Synthesis gas ( $n\text{CO} + m\text{H}_2$ ) which is produced from methane with steam is a raw material for the manufacture of hydrogen, employed in synthesis of ammonia, and, at other ratios of CO to  $\text{H}_2$ ,

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\* Organic chemicals include all carbon compounds except carbon dioxide, its salts and the metal carbides, which are considered to be inorganic in nature.

of saturated and unsaturated hydrocarbons; synthetic alcohols are also made from it.

Chapter 1 of Part II was written by I. Mukhlyonov and A. Amelin, Chapters 2 and 3 were rewritten for the third edition by L. Kuznetsov, Chapters 4 and 5 were written by E. Tumarkina, Chapter 6 by A. Averbukh, Chapter 7 by I. Furmer, Chapter 8 by I. Furmer and A. Amelin, Chapters 9 and 10 by A. Averbukh and Chapter 11 by E. Tumarkina.

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## 1. Properties, Uses and Methods of Production

**Properties.** Anhydrous sulphuric acid (monohydrate),  $\text{H}_2\text{SO}_4$ , is a heavy, oily liquid which mixes with water in all proportions with liberation of large quantities of heat. The density of  $\text{H}_2\text{SO}_4$  at  $0^\circ\text{C}$  is  $1.85\text{ g/cm}^3$ . It boils at a temperature of  $296^\circ\text{C}$  and freezes at  $-10^\circ\text{C}$ .

Commercially not only the monohydrate is known as sulphuric acid, but this name is also applied to its aqueous solutions ( $\text{H}_2\text{SO}_4 + n\text{H}_2\text{O}$ ) and also to solutions of sulphur trioxide in monohydrate

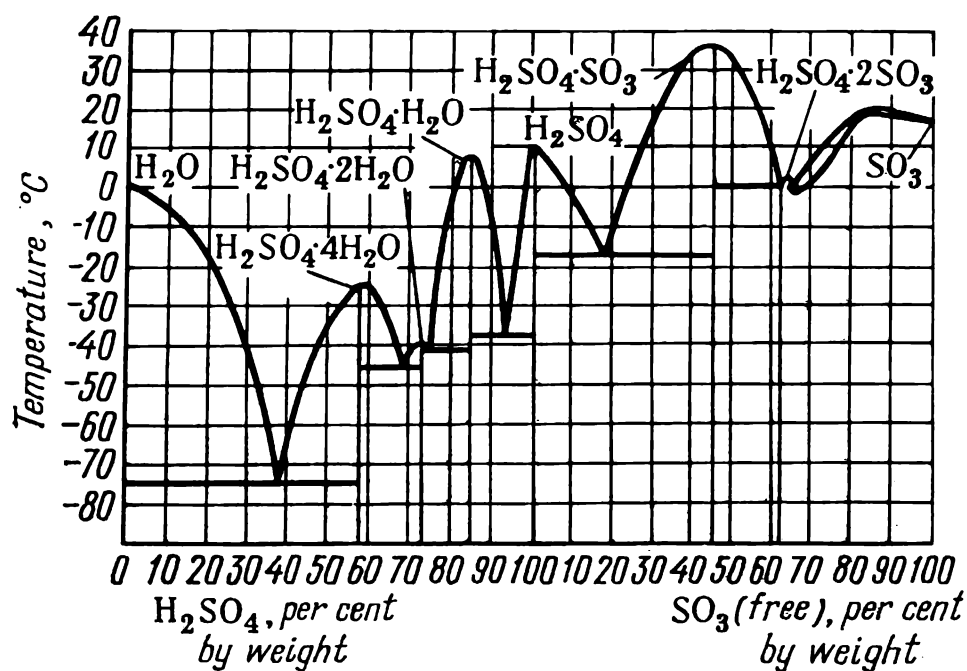


Fig. 1. Phase diagram of crystallization in the  $\text{H}_2\text{O}-\text{SO}_3$  system

( $\text{H}_2\text{SO}_4 + n\text{SO}_3$ ), also described as oleum. Oleum “fumes” when exposed to air due to desorption of  $\text{SO}_3$ . Pure sulphuric acid is a colourless liquid, but the technical product has a dark colour due to impurities present in it.

In manufacturing, transporting and using sulphuric acid the relation between its melting and boiling points, and the concentration are very important. As shown in Fig. 1, when the concentration of sulphuric acid is increased from 0 to 64.35% free  $\text{SO}_3$ , six hydrates are consecutively formed; these are individual chemical compounds

which are mutually insoluble in the solid state and form eutectic mixtures (see Part I, Fig. 61). In the zone of  $\text{SO}_3$ -concentration from 64.35% to 100% crystallization produces solid solutions, i.e. this part of the diagram may be considered to be composed of two separate diagrams (see Part I, Fig. 61). Fig. 1 shows that acids of concentrations close to pure  $\text{SO}_3$ ,  $2\text{SO}_3 \cdot \text{H}_2\text{O}$ ,  $\text{SO}_3 \cdot \text{H}_2\text{O}$  and  $\text{SO}_3 \cdot 2\text{H}_2\text{O}$  cannot be manufactured and used in the winter at low temperatures since this might result in crystallization of the solutions which

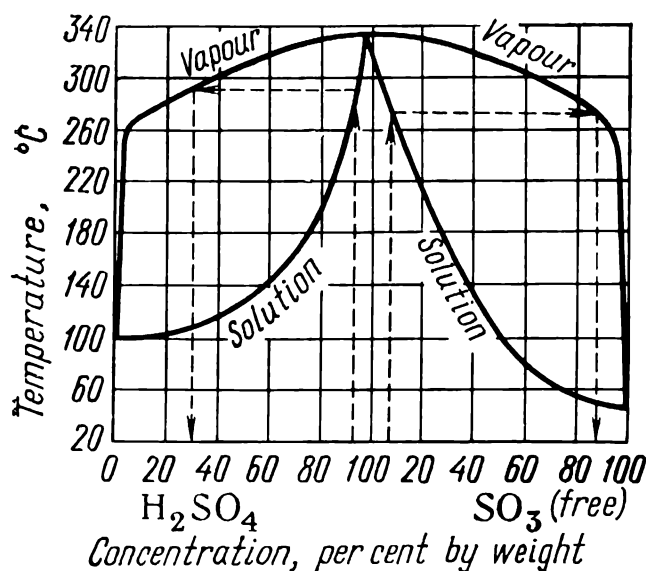


Fig. 2. Boiling diagram of the  $\text{H}_2\text{O}$ - $\text{SO}_3$  system at 1 atm

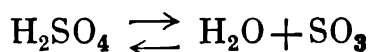
would plug acid lines between shops, storage tanks, pumps, and other unheated apparatus. All commercial grades of sulphuric acid have concentrations close to eutectic compositions.

The vapour-liquid phase equilibrium for  $\text{H}_2\text{O}$ - $\text{SO}_3$  mixtures at atmospheric pressure is shown in Fig. 2. The mixture with a concentration of 98.3%  $\text{H}_2\text{SO}_4$  is azeotropic, i.e. the temperatures at which the vapour condenses and the liquid boils, 336.6 °C, coincide. At a small change in composition in either direction from the azeotropic point the temperature at which vapour conden-

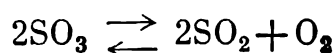
sation begins, called the dew point, differs sharply from the temperature at which the solution boils. Correspondingly, the composition of the liquid phase and that of the vapours above it (or vice versa) also differ sharply.

The vapour-liquid phase diagram of the  $\text{H}_2\text{O}$ - $\text{SO}_3$  system (Fig. 2) is used in determining sulphuric-acid concentrations when water is being evaporated from it. The diagram shows that if acid with a concentration below 80%  $\text{H}_2\text{SO}_4$  is heated, it will boil at a temperature lower than 200 °C and that almost exclusively water will pass over into the vapour phase; only if the concentration of the acid lies above 93% (the dotted line on the diagram) does the  $\text{H}_2\text{SO}_4$  content of the vapour phase increase significantly.

The vapours of sulphuric acid dissociate at high temperatures:



and at temperatures above 400 °C there are already more  $\text{SO}_3$  molecules in the vapours than those of  $\text{H}_2\text{SO}_4$ . Further heating leads to the dissociation of  $\text{SO}_3$



At temperatures above 700 °C  $\text{SO}_2$  is the predominant component of the vapours and above 1000 °C  $\text{SO}_3$  is almost completely dissociated. The degree of dissociation changes with the pressure. This type of thermal dissociation is quite typical for complex chemical compounds. The heat of the reactions which participate in producing sulphuric acid and the intermediate compounds at 298 °K (25 °C) are:

<i>Reaction</i>	<i>kJ/mole</i>	<i>kcal/mole</i>
$\text{S}(\text{gas}) \rightarrow \text{S}(\text{rhombic})$	64.8	15.5
$\text{S}(\text{rhombic}) + \text{O}_2(\text{gas}) \rightarrow \text{SO}_2(\text{gas})$	289	71.0
$\text{SO}_2(\text{gas}) + \frac{1}{2}\text{O}_2(\text{gas}) \rightarrow \text{SO}_3(\text{gas})$	96.1	22.91
$\text{SO}_3(\text{gas}) \rightarrow \text{SO}_3(\text{liquid})$	39.8	9.50
$\text{SO}_3(\text{gas}) + \text{H}_2\text{O}(\text{gas}) \rightarrow \text{H}_2\text{SO}_4(\text{gas})$	125.0	29.83
$\text{H}_2\text{SO}_4(\text{gas}) \rightarrow \text{H}_2\text{SO}_4(\text{liquid})$	50.2	11.98
$\text{H}_2\text{O}(\text{gas}) \rightarrow \text{H}_2\text{O}(\text{liquid})$	44.1	10.52

Sulphuric acid is an extremely active chemical compound. It dissolves the oxides of metals, also most pure metals, and displaces all other acids from their salts at high temperatures. Especially strong is the tendency to combine with water, which results from its capacity to form hydrates. It removes water from other acids, from crystal hydrates of salts, and even from oxygen derivatives of hydrocarbons, which do not contain water as such but contain hydrogen and oxygen in the ratio  $\text{H} : \text{O} = 2$ . Wood and other plant and animal tissues containing cellulose  $(\text{C}_6\text{H}_{10}\text{O}_5)_n$ , starch and sugar decompose in concentrated sulphuric acid; water combines with the acid and only finely-divided carbon remains. In dilute acid cellulose and starch decompose to form sugars. Concentrated sulphuric acid produces acid-burns upon contact with the skin.

**Uses.** The high chemical activity of sulphuric acid combined with the comparatively low cost of manufacturing it has resulted in its use on a tremendous scale and in a great variety of applications. It is hard to find any important branch of the economy in which either sulphuric acid or products made from it are not used. The largest consumption of sulphuric acid is in manufacturing inorganic fertilizers: superphosphate, ammonium sulphate, etc. Many acids (for example, phosphoric, acetic, and hydrochloric acids) and salts are manufactured from sulphuric acid. It is used extensively in manufacturing various non-ferrous and rare metals. In metal processing sulphuric acid or its salts are used for pickling steel items prior to painting, tinning, nickel plating, chrome plating, etc. Large quantities of sulphuric acid are consumed in purifying petroleum products. Processes for manufacturing a number of dyes,



paints and varnishes, pharmaceuticals and some plastics are also based on sulphuric acid. It is used in making ethyl alcohol, some ethers, detergents, a number of insecticides and herbicides. Dilute solutions of sulphuric acid and its salts are used in manufacturing artificial silk and for treating fibres or cloths before dyeing in the textile industry and in other branches of the light industry. In the food industry sulphuric acid is used in manufacturing starch, syrup and a number of other products. Sulphuric-acid lead batteries are used in transportation. It is used for drying gases and in concentrating acids. Finally, sulphuric acid is used in nitrating operations and in manufacturing a large number of explosives.

For nitrating operations, manufacturing ethyl alcohol from ethylene, concentrating nitric acid and in many other cases 92 to 98%  $\text{H}_2\text{SO}_4$  is used and diluted 50-80%  $\text{H}_2\text{SO}_4$  is formed. Such acid is reconcentrated by evaporating water according to the diagram of Fig. 2.

**Manufacturing methods.** Sulphuric acid was manufactured as early as the 13th century, in very small amounts of course, by thermal decomposition of iron vitriol ( $\text{FeSO}_4$ ), and because of this one of the grades of sulphuric acid is still called vitriol oil, although manufacture of sulphuric acid from ferrous sulphate was discontinued many years ago.

Sulphuric acid is now manufactured in two ways: by the nitrous process, which has been in use for more than 200 years, and by the contact process, developed at the end of the 19th and beginning of the 20th centuries. The contact process is replacing the nitrous (tower) one.

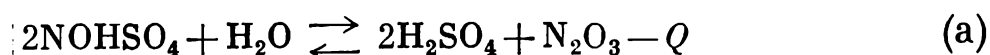
The first stage in manufacturing sulphuric acid by any method is the production of a sulphurous gas by burning a sulphur-containing material. After the sulphurous gas has been purified (especially carefully in the contact method) it is oxidized to sulphur trioxide, which combines with water to form sulphuric acid. Oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  in usual conditions takes place at a very low rate and catalysts are used to accelerate the process.

In the *contact process* for manufacturing sulphuric acid the sulphur dioxide is oxidized to the trioxide over a solid catalyst. Improvements in manufacturing acid by this method have brought the cost of the pure and more concentrated contact sulphuric acid down to just slightly above that of tower acid. Because of this in the USSR only plants using the contact process are now built. At present approximately 80% of all the acid produced is made by the contact method.

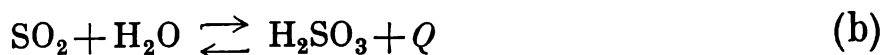
In the *nitrous process* nitrogen oxides are the catalysts. The  $\text{SO}_2$  is oxidized mainly in the liquid phase and the operation is carried out in packed towers. The nitrous process, in accordance with the type of apparatus used, is also known as the *tower process*. In the

tower process after the dust particles (pyrite cinders) are removed from the sulphurous gas obtained by burning a sulphur-containing raw material and with a content of 9%  $\text{SO}_2$  and 9-10%  $\text{O}_2$ , it enters into a system of several (from 4 to 7) packed towers. The temperature at the inlet to the first tower is about 350 °C. In the towers a number of absorption-desorption processes in which chemical conversions are involved take place. A nitrous vitriol solution is fed to the top of the first two or three packed towers; the solution contains dissolved nitrogen oxides which are chemically combined as nitrosyl sulphuric acid,  $\text{NOHSO}_4$ .

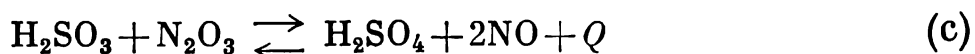
At a high temperature the nitrosyl sulphuric acid is hydrolyzed in the reaction



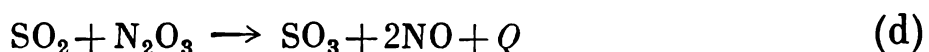
The sulphur dioxide is absorbed by the water and forms sulphurous acid:



the latter reacts with the nitrogen oxides in the liquid phase



The  $\text{SO}_2$  is partially oxidized in the gas phase



The  $\text{SO}_3$  is absorbed by the water and also forms sulphuric acid



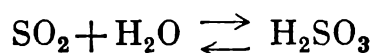
The nitrogen oxide is desorbed into the gas phase and is oxidized to nitrogen dioxide by the oxygen from the air



The nitrogen oxides,  $\text{NO} + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_3$ , are absorbed by sulphuric acid in the following three or four towers by the reverse reaction of equation (a). To accomplish this, the cooled sulphuric acid with a low nitrosyl content which flows out of the first towers is fed to these last towers. When the oxides are absorbed the nitrosyl sulphuric acid which participates in the process is formed. In this way the nitrogen oxides circulate in the system and, theoretically, they are not consumed. Practically, however, due to incomplete absorption some of the nitrogen oxide is lost. The nitrogen oxides consumption, expressed in terms of  $\text{HNO}_3$ , is 10-20 kg per ton monohydrate  $\text{H}_2\text{SO}_4$  produced. The sulphuric acid made by the nitrous method is contaminated with impurities and dilute, with a concentration of 75-77%, and it is mainly employed in making inorganic fertilizers.

## 2. Producing the Roaster Gas

Sulphurous anhydride,  $\text{SO}_2$ , is a colourless gas, 2.3 times heavier than air, with an acrid odour. Pure  $\text{SO}_2$  is liquefied at atmospheric pressure at a temperature of  $-10^\circ\text{C}$ . When dissolved in water it forms the weak, unstable sulphurous acid:



Any substance containing sulphur, either found in nature or a waste product of another manufacturing process, may be used for producing sulphur dioxide (and, consequently, sulphuric acid). In nature sulphur is usually found in one of three forms: (1) elementary native sulphur in a mixture with other minerals; (2) sulphides of metals, for instance iron pyrite,  $\text{FeS}_2$ , copper pyrite,  $\text{FeCuS}_2$ , copper glance,  $\text{Cu}_2\text{S}$ , zinc blende,  $\text{ZnS}$ , and also  $\text{PbS}$ ,  $\text{CoS}$ ,  $\text{NiS}$ , etc.; (3) sulphates: gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , anhydrite,  $\text{CaSO}_4$ , and also  $\text{Na}_2\text{SO}_4$ ,  $\text{MgSO}_4$ , etc.

More than 40% of the sulphuric acid made in the USSR is produced from gases obtained by burning pyrite, consisting of the mineral and admixtures to it. Pure iron pyrite,  $\text{FeS}_2$ , contains 53.5% S and 46.5% Fe. In pyrite the sulphur content usually varies from 35 to 50%, and the iron content from 30 to 40%; the remainder is composed of sulphides of the non-ferrous metals, carbonates, sand, clay, etc. In the USSR there are important pyrite fields in the Ural mountains area, in the Caucasus and in the Central Asia Republics. There are also rich pyrite fields in Spain, Norway, Portugal, Italy and Canada. Pyrite is often found together with the sulphides of non-ferrous metals which are the raw material for manufacturing copper, zinc, lead, nickel, silver, etc. To separate the sulphides of the non-ferrous metals the ore is size-reduced and divided by flotation into concentrates containing the sulphides of the non-ferrous metals and the so-called flotation tails; the latter consist mainly of iron pyrite. Pyrite containing only small amounts of non-ferrous metals is delivered to the plants directly as mined in lumps of various sizes. At the sulphuric-acid manufacturing plants pyrite is crushed in jaw- and roll crushers and then roasted to produce roaster gas.

When sulphides of copper, zinc and other non-ferrous metals are roasted at metallurgical plants gases containing sulphur dioxide are formed which are utilized for manufacturing sulphuric acid. It follows that together with the non-ferrous metals, sulphur dioxide is also produced from the sulphurous ores. More than 25% of the sulphuric acid produced is made from waste gases of non-ferrous metallurgy. A large part of the gases produced in non-ferrous metallurgy have an  $\text{SO}_2$ -content lower than 3%. For making sulphuric acid the gas must first be concentrated. However, at some plants

the gases are not subjected to concentration but are discharged to the atmosphere. At present fuller utilization of the  $\text{SO}_2$ -containing gases of non-ferrous metallurgical plants is planned.

The best raw material for manufacturing sulphur dioxide is sulphur, which is obtained by melting it out of sulphur-containing rock and also as a by-product in manufacturing copper, in purifying industrial gases, etc. Sulphur has a melting point of  $113^\circ\text{C}$ , it ignites easily and can be burned in furnaces of simple design. If sulphur is burned in air the  $\text{SO}_2$  concentration of the gas is higher than of that obtained in roasting pyrite, and the content of undesirable impurities in it is lower.

The cost of the sulphur is several times that of pyrite and therefore only 20% of the sulphuric acid produced in the USSR is made from it, mainly at plants far from sources of pyrite.

Coal always contains sulphur in amounts from 1 to 3 per cent. During combustion of the coal the sulphur is burned and discharged to the atmosphere in the form of  $\text{SO}_2$ . Absorption-desorption methods have been developed for purifying combustion products, in which the  $\text{SO}_2$  is recovered and utilized in manufacturing sulphuric acid.

However the cost of sulphuric acid obtained from such combustion-product gases is several times that of acid made from pyrite, and the amount made in this way is very small. Worldwide the amount of sulphur dioxide discharged to the atmosphere exceeds by more than two times the amount converted into sulphuric acid.

When coal is carbonized or petroleum refined the sulphur contained is partially converted to hydrogen sulphide in the gas phase. When the gas is purified either elementary sulphur or gaseous hydrogen sulphide is obtained; the latter is burned to produce  $\text{SO}_2$ -gas and from it—sulphuric acid.

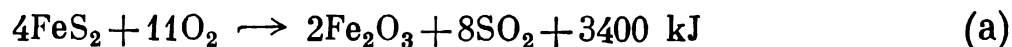
In the Soviet Union there are enormous deposits of calcium sulphate and sodium sulphate which are not yet utilized in the production of sulphuric acid, i.e. they are potential raw material.

When steel is pickled the sulphuric acid used is converted to iron sulphate. When petroleum products are refined there is a residual asphalt, the so-called acid sludge, which contains sulphuric acid. In a number of organic-chemical processes waste-liquor dilute sulphuric acid containing large amounts of organic chemical impurities is produced. These and other similar industrial waste products containing sulphuric acid or its salts, when heated in the presence of reducing agents, yield a sulphurous gas which can be converted to sulphuric acid.

Methods for producing sulphurous gas by roasting the principal raw materials—pyrites, and then by burning sulphur, are discussed in the following paragraphs.

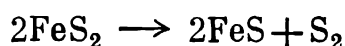
*Iron pyrite is roasted* in air in furnaces of various types at atmospheric pressure. Pyrite oxidation is described by the following overall

equation

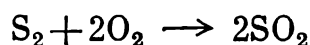


which is used in drawing up material and heat balances. Actually, this irreversible process is comprised of a number of successive and parallel chemical reactions and of diffusion processes which determine the overall process rate at the high temperature.

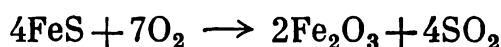
When pyrite is heated to temperatures above 500 °C in the furnace the first process that occurs is pyrite dissociation:<sup>1</sup>



The sulphur quickly burns in the gas phase:



The iron sulphide is oxidized according to the following reaction equation:



Actually below 600 °C oxidation proceeds through formation of sulphates of iron which are intermediate compounds, and at higher temperatures FeO is first formed and then Fe<sub>3</sub>O<sub>4</sub> or Fe<sub>2</sub>O<sub>3</sub>. In all cases when a sulphide is oxidized a thin layer of iron oxides is formed, and further combustion is usually limited by the rate of diffusion of the oxygen of the air into the unoxidized FeS core and the rate of the diffusion of SO<sub>2</sub> from the depth of the grain outward in the opposite direction. It is this inner-diffusion process which limits the overall rate of pyrite roasting.

From 5 to 10% of the sulphur in the pyrite passes into the gas phase as SO<sub>3</sub>. This sulphuric anhydride is produced by oxidation of SO<sub>2</sub>, resulting from the catalytic properties of the cinder, and also by decomposition of sulphates which may have been present in the pyrite or have been formed during its oxidation.

When the pyrite cinder leaves the furnace at high temperatures and when the excess of oxygen in the gas is small, for instance in fluidized-bed roasters, the overall roasting process is described by the following reaction equation:



During the roasting process the sulphides of other metals present in the pyrite are also oxidized, carbonates present decompose, and As<sub>2</sub>O<sub>3</sub>, SeO<sub>2</sub> and all the water contained in the pyrites are transferred to the gas phase. The pyrite cinder consists of oxides of iron, and sulphates and oxides of other metals, quartz, aluminosilicates, and unoxidized FeS. From 0.5 to 2% of the sulphur remains in the cinder.

Experimental data picturing the conversion of the sulphur when pyrite is burned in a stationary-bed furnace are given in Fig. 3.

The optimal roasting conditions can be determined by an analysis of the effect of various operating conditions on the process rate using the equation for the rate of the heterogeneous process:

$$\frac{dG_{\text{SO}_2}}{d\tau} = kF \Delta C \quad (1.1)$$

The driving force of the reaction is raised by an increase in the  $\text{FeS}_2$  content of the pyrite or the oxygen concentration of the gas mixture. This is accomplished by pyrite beneficiation (removing impurities from the  $\text{FeS}_2$ ) by flotation and also by using oxygen-enriched air for roasting. However, these methods of raising the process rate require large expenditures and are, therefore, rarely used. Ordinarily, an excess of air, 1.2-1.8 fold with respect to the stoichiometric amount of equations (a) or (b), is used. The principal reactions are irreversible under the conditions in which roasting is carried out, and, therefore, methods for shifting the equilibrium cannot be used in this case.

An increase in the mass-transfer coefficient,  $k$ , and the process rate can be achieved by raising the temperature, but there is a limit to the temperature rise because of sintering of the pyrite particles into large lumps at temperatures from 850 to 1000 °C, depending on the character of the impurities in the pyrites and the type of roasting furnace.

External diffusion processes are intensified by stirring the pyrites in the air, however, as was mentioned above, the limiting factor of the overall combustion process is diffusion of oxygen and sulphur dioxide inside the pores of the iron-oxide layer on the pyrite particles, which grows as roasting proceeds. Therefore, fine crushing of the pyrite is the most important way to facilitate diffusion and increase the area of contact,  $F$ , of the iron sulphides with the oxygen of the air. Flotation pyrites usually consist mainly of particles from 0.03 to 0.3 mm in diameter and, naturally, for such large differences in size the time necessary for complete sulphur conversion varies by tens of times depending on the particle size. The area

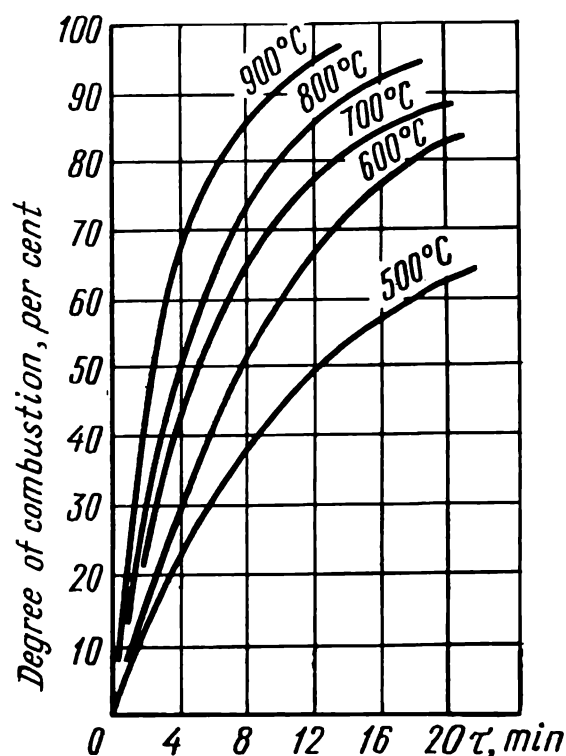


Fig. 3. The degree of combustion of the sulphur in pyrite as a function of temperature

of contact of the pyrite with the air is increased if it is agitated, and the intensity of agitation depends on the type of furnace used.

The roasting products consist of sulphur dioxide, oxygen, nitrogen and admixtures. There must be oxygen in the gas for oxidizing the sulphur dioxide to the trioxide.

The ratio of oxygen to sulphur dioxide, not taking into account the  $\text{SO}_3$  present, can be calculated from

$$C_{\text{O}_2} = n - \left[ m - \frac{n(m-1)}{100} \right] C_{\text{SO}_2} \quad (1.2)$$

where  $C_{\text{O}_2}$  and  $C_{\text{SO}_2}$  are the concentrations of the oxygen and sulphur dioxide in the gas, vol. %;  $m$ —the ratio of the number of oxygen molecules which react to those of sulphur dioxide formed in the reaction (according to the overall reaction equation);  $n$ —the oxygen content of the air or any other oxygen-nitrogen mixture used for combustion, vol. %.

*Furnaces for roasting pyrites* in use in the USSR can be divided into three types: (1) multihearth furnaces in which the pyrites are agitated in the bed, (2) flash roasters in which the pyrites are sprayed into an air stream and (3) fluidized-bed roasters. Furnaces of type (2) and (3) provide maximum area of contact, equal to the total surface area of the particles.

*Multihearth furnaces* (see Part I, Fig. 72) can be used for roasting any finely crushed sulphide material. They are used for roasting flotation pyrite and lump pyrite, sulphide ores of non-ferrous metals and sulphur-containing sludges from gas-purification units. When pyrite is roasted the gas produced contains on the average 9%  $\text{SO}_2$ , 9%  $\text{O}_2$ , and 82%  $\text{N}_2$ .\* The pyrite cinder leaving the furnace has on the average a 2% unoxidized-sulphur content. The operating intensity of roasters averages 225 kg of pyrites per sq. metre of roaster hearth per 24 hours or 185 kg per  $\text{m}^3$  of roaster volume per 24 hours.\*\* Where flotation pyrite is roasted in beds, sintering and formation of lumps may easily occur, and the temperature inside the roasters is, therefore, not allowed to rise above 850-900 °C, depending on the presence of low-melting impurities in the pyrites. High temperatures also result in corrosion and damage to the cast-iron teeth, rakers and even the shaft of the roaster.

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\* In technical calculations the composition of a gas mixture is ordinarily expressed in per cent referred to dry gas since the amount of water vapour in the gas usually varies widely. In this case it depends on the moisture content of the pyrite and the air. The noble gases of the air are arbitrarily added to the nitrogen.

\*\* In calculating the operating intensity the actual amount of pyrite burned is converted to units of dry pyrite containing 45% S. In natural pyrites the sulphur content is usually below 45% and intensity values calculated in terms of the natural pyrites are, therefore, higher than those mentioned.

Mechanical multihearth roasters are of complex design, their operation intensity is low and operating cost high; they do not provide complete combustion of the sulphur in the pyrite and do not produce a high-concentration roaster gas, and they have, therefore, almost everywhere been replaced by roasters of other types.

*Flash roasters* (see Part I, Fig. 74) are used for burning dry flotation pyrite. The entire surface of the pyrite particles, which burn in flight in an air stream, is in contact with the air and, therefore, combustion proceeds at a high rate and sintering does not occur as readily as in multihearth furnaces. The maximum permissible temperature is 1100 °C. This allows the use of a smaller excess of air than in multihearth furnaces. Hence the roaster gas can contain up to 13% SO<sub>2</sub> and the sulphur content of the cinder is from 1 to 1.5%. The roaster combines such features as simple design with operating intensities as high as 700-1000 kg/m<sup>3</sup> per 24 hours. The heat of the roaster gases, which exit at a temperature of 1000 °C, is utilized in waste-heat boilers to produce steam.

The principal drawback of these roasters, which results in their limited use, is that only flotation pyrites containing very little moisture and with a constant sulphur content can be burnt (variations in the pyrite composition cause sharp changes in the composition of the gas; moist pyrite clogs the injector nozzle and disrupts roaster operation). Another fault is that the dust content of the gas is usually above 100 g/m<sup>3</sup>, as compared to 10 g/m<sup>3</sup> for multihearth furnaces.

*Fluidized-bed furnaces* (see Part I, Fig. 75) are used for roasting flotation- and lump pyrites, and other sulphide ores. However, in contrast to multihearth furnaces, particles of sharply differing size cannot be roasted in one and the same furnace. The rate of air flow at which the particles are suspended is approximately proportional to their size, and for the larger particles of lump pyrite the necessary flow rate is tens of times higher than for those of flotation pyrite.

In fluidized-bed roasters, where also the air flows over the entire surface of the particles, the concentration of the particles per unit volume is much higher than in flash roasters, and roaster operating intensity is also higher, 1000 to 1800 kg/m<sup>3</sup> per 24 hours. Gas containing up to 15% SO<sub>2</sub> and pyrite cinder with only 0.5% S can be produced. For utilization of the heat of the reaction tubes of a waste-heat boiler can be located both in the stream of combustion gases and directly within the fluidized bed, where the heat-transfer coefficient is much higher than for transfer from the gas. The amount of steam produced is larger than in flash roasters and can be as much as 1.3 ton/ton pyrites. The temperature is uniform over the bed; it is kept at about 800 °C by removing heat. The amount of dust in the roaster gas is even larger than for flash roasters. Since



they have higher operating intensity, produce roaster-gas with higher  $\text{SO}_2$  concentrations and provide fuller utilization of the sulphur in the pyrites, fluidized-bed roasters have replaced multihearth furnaces in sulphuric-acid production and non-ferrous metallurgy.

*Material and heat balances of pyrite-roasters* are drawn up by the generally used method discussed in Chapter 2, Part I. The material and heat balances of a KC-450 roaster are given as an example.

The data used in the calculations:

Furnace capacity (100% $\text{H}_2\text{SO}_4$ ), $G_{\text{H}_2\text{SO}_4}$ , ton/hr	20.833
Degree of sulphur conversion, $\beta$	0.885
Consumption of dry pyrite (45% S) per ton $\text{H}_2\text{SO}_4$ , $\alpha$ , tons	0.82
Content of (%):	
sulphur in the pyrite, $C_S$	41
moisture in the pyrite, $C_w$	6
sulphur in the cinder, $C_{S(\text{cinder})}$	1
$\text{SO}_2$ in "dry" combustion gases, $C_{\text{SO}_2}$	14.5
$\text{SO}_3$ in "dry" combustion gases, $C_{\text{SO}_3}$	0.1
Temperature, °C:	
pyrite, $t_{\text{pyrite}}$	20
air, $t_{\text{air}}$	20
effluent combustion gases, $t_g$	850
cinder, $t_{\text{cinder}}$	850
Relative humidity of the air, $\phi$ , %	50

Calculations:

Total sulphur content of the pyrite:

$$G_S = \frac{M_S G_{\text{H}_2\text{SO}_4} \cdot 1000}{M_{\text{H}_2\text{SO}_4} \beta} = \frac{32.06 \cdot 20.833 \cdot 1000}{98.08 \cdot 0.885} = 7695 \text{ kg/hr}$$

Dry pyrite:

$$G_{\text{pyrite}} = \frac{G_S \cdot 100}{C_S} = \frac{7695 \cdot 100}{41} = 18\,768 \text{ kg/hr}$$

Content of water in pyrite:

$$G_w = \frac{G_{\text{pyrite}} \cdot C_w}{100 - C_w} = \frac{18\,768 \cdot 6}{100 - 6} = 1198 \text{ kg/hr}$$

Cinder produced:

$$\begin{aligned} G_{\text{cinder}} &= \frac{160 - C_S}{160 - C_{S(\text{cinder})}} \cdot G_{\text{pyrite}} = \frac{160 - 41}{160 - 1} \cdot 18\,768 = \\ &= 0.748 \cdot 18\,768 = 14\,038 \text{ kg/hr} \end{aligned}$$

Sulphur content of cinder

$$G_{S(\text{cinder})} = \frac{G_{\text{cinder}} \cdot C_{S(\text{cinder})}}{100} = \frac{14\,038 \cdot 1}{100} = 140 \text{ kg/hr}$$

Sulphur lost with cinder:

$$\frac{G_{\text{Scinder}} \cdot 100}{G_S} = \frac{140 \cdot 100}{7695} = 1.82\%$$

Sulphur transferred to gas phase:

$$G'_S = G_S - G_{S(\text{cinder})} = 7695 - 140 = 7555 \text{ kg/hr}$$

Total volume of  $\text{SO}_2 + \text{SO}_3$  produced:

$$V_{(\text{SO}_2 + \text{SO}_3)} = \frac{(G_S - G_{S(\text{cinder})}) \cdot 22.4}{M_S} = \frac{7555 \cdot 22.4}{32.06} = 5279 \text{ m}^3/\text{hr}$$

Volume of  $\text{SO}_2$ :

$$V_{\text{SO}_2} = \frac{V_{(\text{SO}_2 + \text{SO}_3)} C_{\text{SO}_2}}{C_{\text{SO}_2} + C_{\text{SO}_3}} = \frac{5279 \cdot 14.5}{14.5 + 0.1} = 5243 \text{ m}^3/\text{hr}$$

Volume of  $\text{SO}_3$ :

$$V_{\text{SO}_3} = V_{(\text{SO}_2 + \text{SO}_3)} - V_{\text{SO}_2} = 5279 - 5243 = 36 \text{ m}^3/\text{hr}$$

Oxygen concentration of the roaster gas:

$$C_{\text{O}_2} = n - \left[ m - \frac{n(m-1)}{100} \right] C_{\text{SO}_2} - \left[ m + 0.5 \frac{n(m-0.5)}{100} \right] C_{\text{SO}_3}$$

where  $n$  is the oxygen content of the air,  $n = 21\%$ ;  $m$ —the stoichiometric ratio of oxygen to sulphur dioxide.

For the given reaction equation  $4\text{FeS}_2 + 11\text{O}_2 = 8\text{SO}_2 + 2\text{Fe}_2\text{O}_3$

$$m = \frac{11}{8} = 1.375$$

$$\begin{aligned} C_{\text{O}_2} &= 21 - \left[ 1.375 - \frac{21(1.375-1)}{100} \right] 14.5 - \\ &\quad - \left[ 1.375 + 0.5 \frac{21(1.375-0.5)}{100} \right] 0.1 = 2.06\% \end{aligned}$$

The total volume of dry roaster gas:

$$V_g = \frac{V_{\text{SO}_2} \cdot 100}{C_{\text{SO}_2}} = \frac{5243 \cdot 100}{14.5} = 36159 \text{ m}^3/\text{hr}$$

The volume of oxygen in the roaster gas:

$$V_{\text{O}_2} = \frac{V_g C_{\text{O}_2}}{100} = \frac{36159 \cdot 2.057}{100} = 744 \text{ m}^3/\text{hr}$$

The volume of nitrogen in the roaster gas:

$$\begin{aligned} V_{\text{N}_2} &= V_g - (V_{\text{SO}_2} + V_{\text{SO}_3} + V_{\text{O}_2}) = 36159 - (5243 + 36 + 744) = \\ &= 30136 \text{ m}^3/\text{hr} \end{aligned}$$

The volume of dry air fed to the roaster (air contains 79% N<sub>2</sub>):

$$V_{\text{air}} = \frac{V_{\text{N}_2} \cdot 100}{C_{\text{N}_2}} = \frac{30\,136 \cdot 100}{79} = 38\,147 \text{ m}^3/\text{hr}$$

Material Balance of a KC-450 Roaster

In			Out		
Item	amount		Item	amount	
	kg	m <sup>3</sup>		kg	m <sup>3</sup>
Dry pyrite	18 768	—	Cinder	14 038	—
Pyrite moisture	1 198	—	Roaster gas:		
Dry air	49 400	38 147	SO <sub>2</sub>	15 337	5 243
Moisture in air	358	445	SO <sub>3</sub>	129	36
			O <sub>2</sub>	1 063	744
			N <sub>2</sub>	37 600	30 136
			H <sub>2</sub> O	1 556	1 936
Total	69 724	38 592	Total	69 724	38 095

The volume of the water vapour (at 20 °C and relative humidity φ = 50% the partial pressure of the water vapour is P<sub>H<sub>2</sub>O</sub> = 8.77 mmHg):

$$V'_{\text{H}_2\text{O}} = \frac{V_{\text{air}} P_{\text{H}_2\text{O}}}{760 - P_{\text{H}_2\text{O}}} = \frac{38\,147 \cdot 8.77}{760 - 8.77} = 445 \text{ m}^3/\text{hr}$$

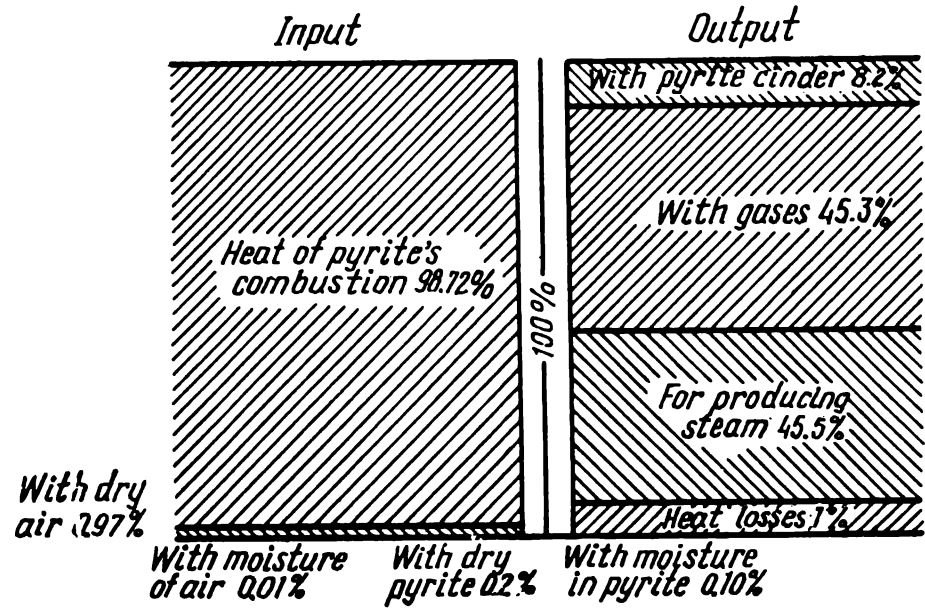


Fig. 4. Diagram of a KC-450 furnace heat balance

The total volume of the water vapour in the roaster gas:

$$V_{\text{H}_2\text{O}} = \frac{G_{\text{w}} \cdot 22.4}{M_{\text{H}_2\text{O}}} + V'_{\text{H}_2\text{O}} = \frac{1198 \cdot 22.4}{18} + 445 = 1936 \text{ m}^3/\text{hr}$$

The heat balance of the roaster, calculated from the data of the material balance using the equations of Part I, Chapter 2, is summed up in the following table.

Heat Balance of a KC-450 Roaster

In			Out		
Item	amount		Item	amount	
	10 <sup>-3</sup> kJ	%		10 <sup>-3</sup> kJ	%
Heat with dry pyrite	204	0.20	Heat with cin-der	8 380	8.2
Heat with the pyrite moi-sture	101	0.10	Heat with ro-aster gas	46 128	45.3
Heat with dry air	993	0.97	Heat losses	1 022	1.0
Heat with air moisture	13.4	0.01	Heat consu-med in ge-nerating steam in the fluidized bed	46 437	45.5
Heat of pyrite combustion	100 656	98.72			
Total	~ 101 967	100	Total	101 967	100

As can be seen from the balance, the heat of pyrite combustion is the predominant heat source, and all the others may be neglected in approximate calculations.

The table includes only heat used for generating steam directly inside the fluidized bed. However, steam is also generated at the expense of the heat of the roaster gas leaving the furnace. Hence, a large fraction of the heat of combustion of the pyrite is utilized effectively. This is illustrated by the heat-balance diagram of Fig. 4.

*Calculation of the Basic Characteristics of a KC-450 Roaster*

The data used in the calculations:	
Depth of the fluidized bed in static conditions, $H_0$ , m	1.0
Roaster operating intensity, $I$ , kg/m <sup>2</sup> /24 hr	10 000
Amount of roasted dry pyrite, containing 41% S, $G_{\text{pyrite}}$ , kg/hr	18 768
Roaster gas temperature, °C:	
at waste-heat boiler entrance, $t_{\text{in}}$	850
at waste-heat boiler exit, $t_{\text{out}}$	450
Heat capacity of roaster gas, $c_g$ , kJ/m <sup>3</sup>	1.43

The furnace diameter is found using

$$F = \frac{\pi D^2}{4} = \frac{24G'}{I}$$

where  $F$  is the area of the roaster hearth,  $\text{m}^2$ ;  $G'$  the amount of dry pyrite (45% S) roasted, as found from

$$G' = \frac{G_{\text{pyrite}} C_S}{45} = \frac{18\,768 \cdot 41}{45} = 17\,100 \text{ kg/hr}$$

$$D = \sqrt{\frac{4 \cdot 24 G'}{\pi I}} = \sqrt{\frac{4 \cdot 24 \cdot 17\,100}{3.14 \cdot 10\,000}} = 7.3 \text{ m}$$

Amount of heat utilized in the waste-heat boiler (if heat losses in the boiler amount to 1%) is determined as follows:

$$Q_b = V c_g (t_{\text{in}} - t_{\text{out}}) 0.99 = 38\,095 \cdot 1.43 (850 - 450) 0.99 = 21\,500\,000 \text{ kJ/hr}$$

Total amount of heat utilized (in the KC roaster and waste-heat boiler) is [taking into account that  $Q_r = 46\,437\,000 \text{ kJ/hr}$  (see the heat balance)]:

$$Q_{\text{total}} = Q_r + Q_b = 46\,437\,000 + 21\,500\,000 = 67\,937\,000 \text{ kJ/hr}$$

Steam generated:

$$\text{St} = \frac{Q_{\text{total}}}{q} = \frac{67\,937\,000}{2790} = 24\,400 \text{ kg/hr}$$

$q$  being the enthalpy of the steam at 40 atm gauge;  $q = 2790 \text{ kJ/hr}$ .

Steam generated per ton  $\text{H}_2\text{SO}_4$ :

$$\text{St} = \frac{24\,400}{20.833} = 1167 \text{ kg/ton } \text{H}_2\text{SO}_4$$

or 1.17 ton/ton  $\text{H}_2\text{SO}_4$ .

The production capacity of roasters being put into operation is growing continuously; roaster unit production capacity has already risen to 1000 ton per day. The calculation methods given above can be used regardless of the roaster size.

*Sulphur can be burned simpler and easier than pyrite. The reaction is*



Actually the sulphur melts before it burns ( $t_{\text{melting point}} \cong \cong 113^\circ\text{C}$ ), evaporates ( $t_{\text{boiling point}} \cong 444^\circ\text{C}$ ) and burns in the gas phase. It follows that the combustion process is in fact homogeneous.

Calculation of the gas composition using equation (1.2) is simpler when sulphur is burned, since  $m=1$ . When sulphur is burned in air ( $n = 21$ )

$$C_{\text{O}_2} = 21 - C_{\text{SO}_2} \quad (1.3)$$

i.e. by theory the  $\text{SO}_2$  content of the gas can be 21%. Actually an excess of air is used; in sulphuric acid production the roaster gas contains about 12%  $\text{SO}_2$  and in making pulp—up to 16%  $\text{SO}_2$ .

For burning pure sulphur most often injection (Fig. 5) and cyclone furnaces are used. The sulphur is first melted with steam in a melting kettle, filtered, and then sprayed into the furnace through nozzles by compressed air; the sulphur evaporates and burns. In injection furnaces mixing of the sulphur and the air is poor, the rate is limited by diffusion and burning is not intensive.

In cyclone furnaces, due to the tangential air feed, there is extremely effective mixing of the sulphur vapour with the air and the

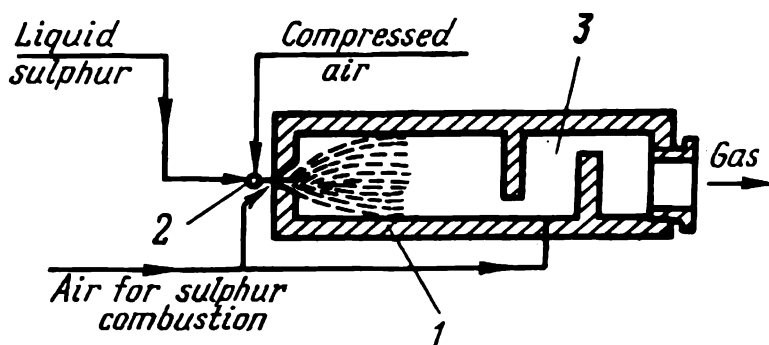


Fig. 5. An injector type sulphur burner:

1—steel shell with lining; 2—injector-nozzles; 3—chamber for final sulphur combustion

intensity of the combustion process is much higher. Because of this cyclone furnaces are now widely replacing injection furnaces.

*Entrained dust must be removed from the roaster gases to prevent it from clogging downstream apparatus and from polluting the acid.* The gases leaving the furnace may contain from 10 to 300 g pyrite-cinder dust per cubic metre of gas. Preliminary removal is carried out in cyclone separators or in inertia-type dedusters which are used with fluidized-bed and flash roasters, since in these roasters dust entrainment is large. After the preliminary dust-separation the gas is passed over the tubes of a waste-heat boiler, which produces high-pressure steam. Final dedusting, to a content of 0.1 g/m<sup>3</sup>, is carried out in electrostatic filters.

### 3. The Contact Process for Manufacturing Sulphuric Acid

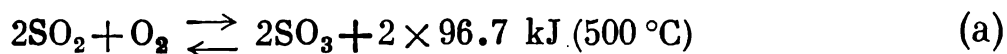
The contact process produces a number of grades of sulphuric acid: oleum containing 20% free SO<sub>3</sub>, vitriol oil (92.5% H<sub>2</sub>SO<sub>4</sub> and 7.5% H<sub>2</sub>O), battery acid, which has approximately the same concentration as vitriol oil but is of higher purity.

The contact process for manufacturing sulphuric acid consists of three stages: (1) separation of impurities which are harmful to the catalyst from the gas, (2) catalytic oxidation of SO<sub>2</sub> to SO<sub>3</sub>, (3) absorption of SO<sub>3</sub> to produce the sulphuric acid.

The principal stage is that of catalytic oxidation of SO<sub>2</sub> to SO<sub>3</sub>; and the name of the method stems from this operation, called contacting.

*Catalytic oxidation* of  $\text{SO}_2$  is a typical example of heterogeneous, exothermic oxidation catalysis. It is one of the most thoroughly studied of all catalytic reactions. In the USSR the most important fundamental studies of oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  and development of catalysts for the reaction were carried out by G. K. Boreskov.

The equilibrium of the reversible reaction



according to the Le Chatelier principle can be shifted to the right (formation of  $\text{SO}_3$ ) by lowering the temperature and increasing the pressure; this results in a corresponding increase in the degree of conversion of  $\text{SO}_2$  to  $\text{SO}_3$  at equilibrium:

$$x_e = \frac{G^*}{G_{\max}} = \frac{p_{\text{SO}_3}^*}{p_{\text{SO}_2}^* + p_{\text{SO}_3}^*} \quad (1.4)$$

where  $G^*$  is the amount of  $\text{SO}_3$  produced at equilibrium;  $G_{\max}$ —the maximum possible amount of  $\text{SO}_3$ , obtained when the  $\text{SO}_2$  is completely converted into  $\text{SO}_3$  by reaction (a);  $p_{\text{SO}_2}^*$  and  $p_{\text{SO}_3}^*$  are the equilibrium partial pressures of  $\text{SO}_2$  and  $\text{SO}_3$  or the equilibrium volume concentrations\*.

Raising the pressure leads to an increase in the rate of reaction (a). Equilibrium yields are determined quantitatively using the equilibrium constant, which in textbooks and reference books on manufacturing sulphuric acid is defined as the square root of what is usually considered to be the equilibrium constant [see Part I, equation (2.13)]:

$$K_1 = \sqrt{K_e} = \sqrt{\frac{(p_{\text{SO}_3}^*)^2}{(p_{\text{SO}_2}^*)^2 \cdot p_{\text{O}_2}^*}} = \frac{p_{\text{SO}_3}^*}{p_{\text{SO}_2}^* \cdot \sqrt{p_{\text{O}_2}^*}} \quad (1.5)$$

or, when recalculated in terms of initial  $\text{SO}_2$  and  $\text{O}_2$  concentrations ( $p_{\text{SO}_2}$ ) and ( $p_{\text{O}_2}$ ):

$$K_1 = \frac{x_e}{1 - x_e} \cdot \frac{1}{\sqrt{\frac{p_{\text{O}_2} - 0.5 p_{\text{SO}_2} x_e}{P (100 - 0.5 p_{\text{SO}_2} x_e)}}} \quad (1.6)$$

where  $P$  is the overall gas pressure, usually 1 atm.

The relationship between  $K_1$  and the temperature within the interval of temperatures common for industrial conditions, given in Fig. 6, is computed using the van't Hoff equation [see Part I, (2.26)].

The equilibrium conversion,  $x_e$ , is usually computed from the values for  $K_1$  which are listed in tables in handbooks and textbooks on sulphuric acid. Transformed equation (1.6) for  $P = 1$  atm is

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\* The equilibrium volume concentration is denoted by  $C^*$ .

used:

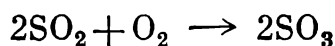
$$x_e = \frac{K_1}{K_1 + \sqrt{\frac{100 - 0.5p_{\text{SO}_2}x_e}{p_{\text{O}_2} - 0.5p_{\text{SO}_2}x_e}}} \quad (1.7)$$

From (1.7)  $x_e$  is computed by successive substitution of the preliminarily computed value of  $x_e$  in the expression under the square root sign until the right-hand side of the equation becomes equal to the left-hand side.

For usual compositions of the gas mixture (7%  $\text{SO}_2$  and 11%  $\text{O}_2$ ) the equilibrium constant is large enough to give  $x_e > 97\%$  at temperatures below  $450^\circ\text{C}$ ; when the temperature is raised above this value  $K_1$  and  $x_e$  drop sharply. However, in the early stages of the oxidation process, even if high-activity catalysts are used, the temperature must be raised above  $450^\circ\text{C}$  to increase the reaction rate.

Hundreds of substances have been found which accelerate the rate of  $\text{SO}_2$ -oxidation, but only the three best catalysts have been used commercially; they are: (1) metallic platinum, (2) ferric oxide, (3) vanadium pentoxide.

The effects caused by these catalysts can be used to show how a decrease in the activation energy and a diminished reaction order influence a process rate. According to the equation



the rate of the homogeneous non-catalytic forward reaction of  $\text{SO}_2$ -oxidation should be expressed by a third-order equation ( $n = 2 + 1 = 3$ )

$$\vec{u} = \frac{dC_{\text{SO}_3}}{d\tau} = k_1 C_{\text{SO}_2}^2 C_{\text{O}_2} \quad (1.8)$$

where  $C_{\text{SO}_3}$ ,  $C_{\text{SO}_2}$ , and  $C_{\text{O}_2}$  are the current concentrations at a given moment.

And the reaction does, actually, take place at an extremely small rate due to the low probability of a three-molecule collision and the very high activation-energy value,  $E \geq 280 \text{ kJ/g-mole SO}_3$ .

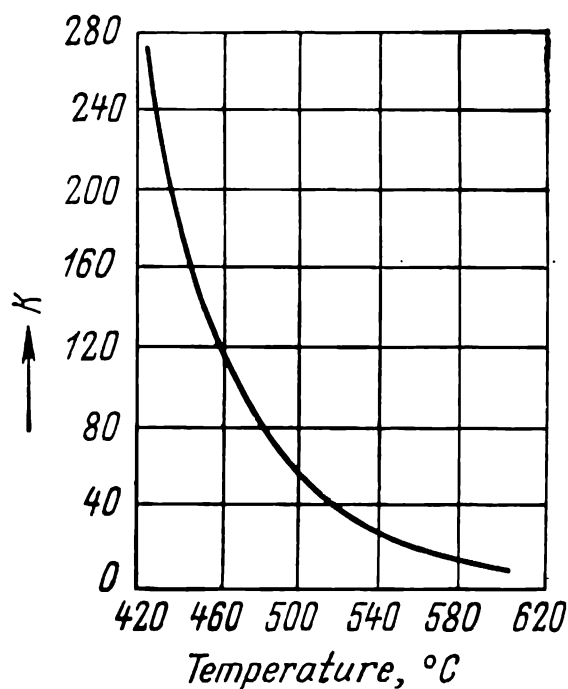


Fig. 6. Equilibrium constant  $K$  as a function of temperature ( $P = 1 \text{ atm}$ )



The rate of the forward reaction over a ferric catalyst ( $\text{Fe}_2\text{O}_3$ ) is expressed by

$$\vec{u} = \frac{dC_{\text{SO}_3}}{d\tau} = k_c \left( \frac{C_{\text{SO}_2}}{C_{\text{SO}_3}} \right)^{1.5} C_{\text{O}_2} \quad (1.9)$$

according to which the reaction order is lowered to  $n = 1.5 + 1 = 2.5$  and the activation energy is  $E_c = 160$  kJ/g-mole with the ignition temperature high— $t_1 > 600\text{--}650^\circ\text{C}$  depending on the  $\text{O}_2 : \text{SO}_2$  ratio of the gas mixture.

For vanadium catalysts with a potassium activator ( $n\text{V}_2\text{O}_5 + m\text{K}_2\text{O}$ ) in ordinary catalysis conditions the approximate Boreskov equation can be employed; it expresses the overall reaction rate through

$$\vec{u} = \frac{dC_{\text{SO}_3}}{d\tau} = k_c \left( \frac{C_{\text{SO}_2} - C_{\text{SO}_2}^*}{C_{\text{SO}_3}} \right)^{0.8} C_{\text{O}_2} \quad (1.10)$$

with  $n = 0.8 + 1 = 1.8$  and  $E_c = 92$  kJ/g-mole at  $t_1 > 400^\circ\text{C}$ .

Equation (1.10) is not accurate for low degrees of oxidation (low  $x$  values) and high temperatures.

Boreskov also gave a more exact equation, which is applicable over wide limits of  $C_{\text{SO}_2}$ ,  $C_{\text{O}_2}$  and  $x$ :

$$u = k_c C_{\text{O}_2} \frac{C_{\text{SO}_2}}{C_{\text{SO}_2} + 0.7 C_{\text{SO}_3}} \left[ 1 - \left( \frac{C_{\text{SO}_3}}{C_{\text{SO}_2} C_{\text{O}_2}^{1/2} K_e} \right)^2 \right] \quad (1.11)$$

However, an analysis of the mechanism of the catalytic process and also approximate calculations can be made more easily using (1.10) and, therefore, it will be employed below.

For the most active, platinum, catalyst (metal platinum)

$$u = \frac{dC_{\text{SO}_3}}{d\tau} = k_c \frac{C_{\text{SO}_2} - C_{\text{SO}_2}^*}{\sqrt{C_{\text{SO}_3}}} \quad (1.12)$$

where  $C_{\text{SO}_2}^*$  is the equilibrium  $\text{SO}_2$ -concentration;  $n = 1$  and  $E_c = 68$  kJ/g-mole at  $t_1 < 350^\circ\text{C}$ . That the rate of the catalytic process depends on the  $\text{SO}_3$  concentration of the gas ( $C_{\text{SO}_3}$ ) shows that the process is limited by desorption of the  $\text{SO}_3$  formed on the catalyst surface.

The catalyst activity is calculated from

$$A_c = \frac{k_c}{k} = e^{\frac{\Delta E}{RT}} \quad (1.13)$$

where  $\Delta E = E - E_c$ .

The most active catalyst is platinum, however it is no longer used because of its high cost and because it is easily poisoned by impurities in the roaster gas, especially by arsenic. Ferric oxide costs less and is not poisoned by arsenic, but for the usual gas com-

position—7%  $\text{SO}_2$  and 11%  $\text{O}_2$ , it acts as a catalyst only at temperatures above 625 °C, i.e. when  $x_e < 70\%$  and it has, therefore, been used only for carrying out the initial stages of  $\text{SO}_2$ -oxidation, to reach  $x_e = 50\text{--}60\%$ . Vanadium catalysts are less active than platinum, but they cost less and poisoning by arsenic compounds is several thousand times lower than with a platinum catalyst; they were found to be the best catalysts and at present are the only ones used for manufacturing sulphuric acid. The vanadium catalytic material contains on the average 7%  $\text{V}_2\text{O}_5$ ; oxides of the alkaline metals serve as promoters, usually a  $\text{K}_2\text{O}$ -promotor is used; porous aluminosilicate is employed as the carrier. Commonly, vanadium catalysts are shaped into porous granules, tablets or rings.

In the conditions of catalysis the potassium oxide is converted to  $\text{K}_2\text{S}_2\text{O}_7$  and the catalyst changes to a porous carrier whose outer surface and pores are wetted with a film of a solution of vanadium pentoxide in liquid potassium pyrosulphate.

Vanadium catalysts are employed at temperatures from 400 to 600 °C. If the temperature is raised above 600 °C the catalyst activity is irreversibly reduced, due to sintering of the active components and formation of inactive ones, which are not soluble in potassium pyrosulphate. If the temperature is lowered the activity of the catalyst drops sharply as a result of transformation of the pentavalent vanadium to the tetravalent state and formation of low-activity vanadyl sulphate,  $\text{VOSO}_4$ . This process is reversible and the higher the  $\text{SO}_2 : \text{O}_2$  ratio of the gas, the higher is the temperature for  $\text{VOSO}_4$  formation, i.e. the ignition temperature  $t_i$ . In industrial conditions at the final stages of  $\text{SO}_2$ -oxidation, where  $\text{O}_2 : \text{SO}_2 > 30$ , the temperature is below 400 °C, and in the first stages of oxidation, if the gas used has a high  $\text{SO}_2$ -concentration, it reaches 500 °C. For an ordinary gas, containing 7%  $\text{SO}_2$  and 11%  $\text{O}_2$ , the ignition temperature at the initial stage of oxidation is about 440 °C, at which temperature the activation energy drops sharply, from  $E = 188 \text{ kJ/g-mole SO}_3$  (over vanadyl sulphate) to  $92 \text{ kJ/g-mole SO}_3$  (over  $\text{V}_2\text{O}_5 + \text{K}_2\text{O}$ ).

The catalytic process has the following stages: (1) diffusion of the reactant component from the core of the gas stream to the pellets and then into the pores of the catalyst; (2) sorption of oxygen by the catalyst (transfer of electrons from the catalyst to oxygen atoms); (3) sorption of  $\text{SO}_2$  molecules to form a complex— $\text{SO}_2 \cdot \text{O} \cdot \text{catalyst}$ ; (4) regrouping of the electrons to form a  $\text{SO}_3 \cdot \text{catalyst}$  complex; (5) desorption of  $\text{SO}_3$  and (6)  $\text{SO}_3$ -diffusion out of the pores of the catalyst and away from the surface of the pellets.

For large-sized grains the overall rate of the process depends on the rate of diffusion of the reactants (stages 1 and 6). Usually pellets no larger than 5 mm in cross section are employed and under these conditions the process is mainly diffusion controlled in the

first stages of  $\text{SO}_2$ -oxidation, and kinetics controlled at the end (at  $x > 80\%$ ). The overall rate of the kinetics-controlled process, referred to unit volume of the vanadium catalyst [see Part I, (2.40)], is given by Boreskov's kinetics equation (1.10), which applies to plug flow reactors:

$$u = \frac{dC_{\text{SO}_3}}{d\tau} = k_c \Delta C = k_c \left[ \frac{C_{\text{SO}_2} - C_{\text{SO}_2}^*}{C_{\text{SO}_3}} \right]^{0.8} C_{\text{O}_2}$$

where  $C_{\text{SO}_3}$ ,  $C_{\text{SO}_2}$ ,  $C_{\text{O}_2}$  are the current concentrations at a given moment, and  $C_{\text{SO}_2}^*$  is the equilibrium concentration. If initial concentrations are substituted for the current ones the kinetics equation transforms into

$$\frac{dx}{d\tau} = k_c \frac{(x_e - x)^{0.8}}{C_{\text{SO}_2} x^{0.8}} \left( C_{\text{O}_2} - \frac{C_{\text{SO}_2} x}{2} \right) \quad (1.14)$$

where  $C_{\text{SO}_2}$ ,  $C_{\text{O}_2}$  are the initial concentrations;  $x$  the degree of  $\text{SO}_2$ -conversion;  $\tau$  is the fictive time of contact between the gas and the catalyst, calculated by dividing the catalyst volume,  $v_c$ , by the volume of gas,  $V_g$  passed through the apparatus in unit time:

$$\tau = \frac{v_c}{V_g} \quad (1.15)$$

Boreskov and Slin'ko have developed a method for the mathematical modelling of catalytic reactors using equations (1.14) and (1.15).

Using equations (1.10) or (1.11) the velocity constant,  $k_c$ , is determined from experimental data by graphical integration methods; in designing calculations, the value of  $\tau$  is determined from the known  $k_c$  value. Then the necessary volume of catalyst,  $v_c$ , to provide the desired apparatus capacity,  $V_g$ , is found [see Part I, (6.18)] with the reserve factor at 1.3 to 2.0.

Equation (1.10) is convenient for analyzing the influence of the process variables on the reaction. From consideration of the expression for the driving force of the process:

$$\Delta C = \left( \frac{C_{\text{SO}_2} - C_{\text{SO}_2}^*}{C_{\text{SO}_3}} \right)^{0.8} C_{\text{O}_2} \quad (1.16)$$

it can be seen that the oxygen concentration exerts the largest influence. Consequently in the catalysis process the slowest stage is that of oxygen sorption. To increase oxygen sorption the oxygen concentration in the gas should be increased, but if the gas is diluted with air the  $\text{SO}_2$ -concentration, and the apparatus capacity, are decreased. Therefore, the optimum concentration of  $\text{SO}_2$  in the gas has been found to be 9%  $\text{SO}_2$  for burning sulphur in air and 7%  $\text{SO}_2$  (at 11%  $\text{O}_2$ ) for roasting pyrite. As the reaction proceeds  $C_{\text{SO}_2}$

increases and  $C_{\text{SO}_2}$  decreases and  $\Delta C$  and the overall process rate,  $u$ , therefore drop logarithmically (see Part I, Fig. 2).

A rise in the temperature leads to an increase in  $C_{\text{SO}_2}^*$ , and a corresponding decrease in  $\Delta C$ . However, according to the Arrhenius equation,  $k_c$  grows with the temperature (see Part I, (2.86)). Therefore, in the early stages of the process, when the degree of  $\text{SO}_2$ -oxidation is low, an increase in the temperature increases the process rate (see Part I, Fig. 16), and when the actual yield approaches the equilibrium value the influence of  $C_{\text{SO}_2}^*$  becomes predominant and the rate of the process drops if the temperature is raised further.

Equations (1.9)-(1.14) relate to reactors with roughly ideal plug flow. They can, for instance, be successfully employed for technological calculations of catalytic reactors with a filtering catalyst bed. The presence of some axial mixing of the gas in the apparatus, which lowers the value of  $\Delta C$ , is accounted for by the reserve factor of equation

$$v_c = \xi V \tau$$

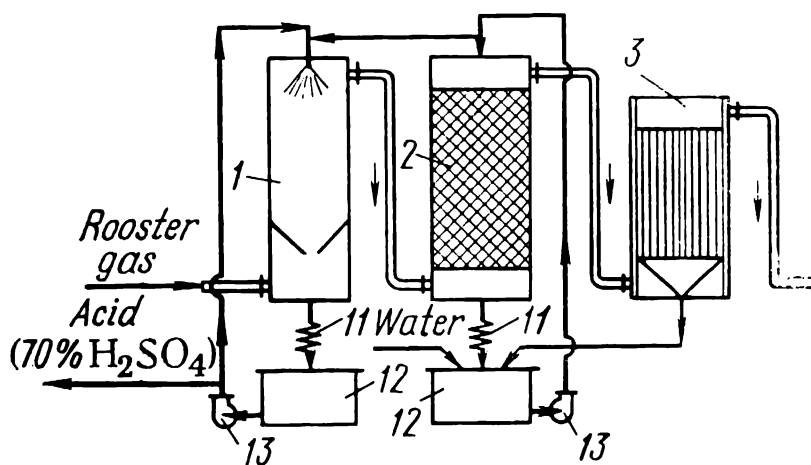
which is employed in computing the amount of catalyst necessary.

In fluidized-bed catalytic reactors there is mixing of the gas and channeling of large bubbles; the calculations can be carried out using a complete-mixing model, i.e. the left-hand side of equation (1.14) is expressed as  $x/\tau$  (instead of  $dx/d\tau$ ). On the other hand, in a fluidized bed of a small-grain catalyst diffusional braking is lower and temperature conditions are optimal and, therefore, the catalyst reserve-factor  $\xi$  is reduced.

For a given time of contact between the gas and the catalyst a maximum  $\text{SO}_3$  yield is achieved at a certain, optimal, temperature. The lower the time of contact  $\tau$  (and, correspondingly,  $x_{\text{SO}_3}$ ) the higher will the optimal temperature be (see Part I, Fig. 94). It follows that for achieving maximum process rates in the contacting apparatus the process should be started at a maximum temperature, about 600 °C, proceed along the optimal-temperature curve and end at 400 °C. Preliminary heating of the gas and continuous heat removal as the reaction proceeds are necessary to achieve these conditions. The design of modern contacting apparatus is determined by these demands; however, modern designs do not represent an ideal solution. Fresh gas containing  $\text{SO}_2$  is heated by interchange with the gas leaving the reactor (utilization of the heat of reaction) only to the ignition temperature (440-450 °C), and then during the catalytic reaction the temperature at first rises almost to 600 °C, after which it is lowered. In a tubular apparatus (see Part I, Fig. 109), heat is removed continuously, but such apparatus was found difficult to operate. Shelf-type apparatus (see Part I, Fig. 105) with stagewise heat removal in heat exchangers located between the shelves is used more often. For gas with higher  $\text{SO}_2$ -concentrations

Fig. 7. Flow diagram of sulphuric acid manufacture by a catalytic process:

1—first scrubber tower; 2—second packed scrubber tower; 3—wet electrostatic filter; 4—packed drying tower; 5—turbocompressor; 6—shell-and-tube heat exchanger; 7—catalytic reactor; 8—shell-and-tube gas cooler; 9 and 10—packed absorption towers; 11—acid coolers; 12—acid tanks; 13—centrifugal pumps

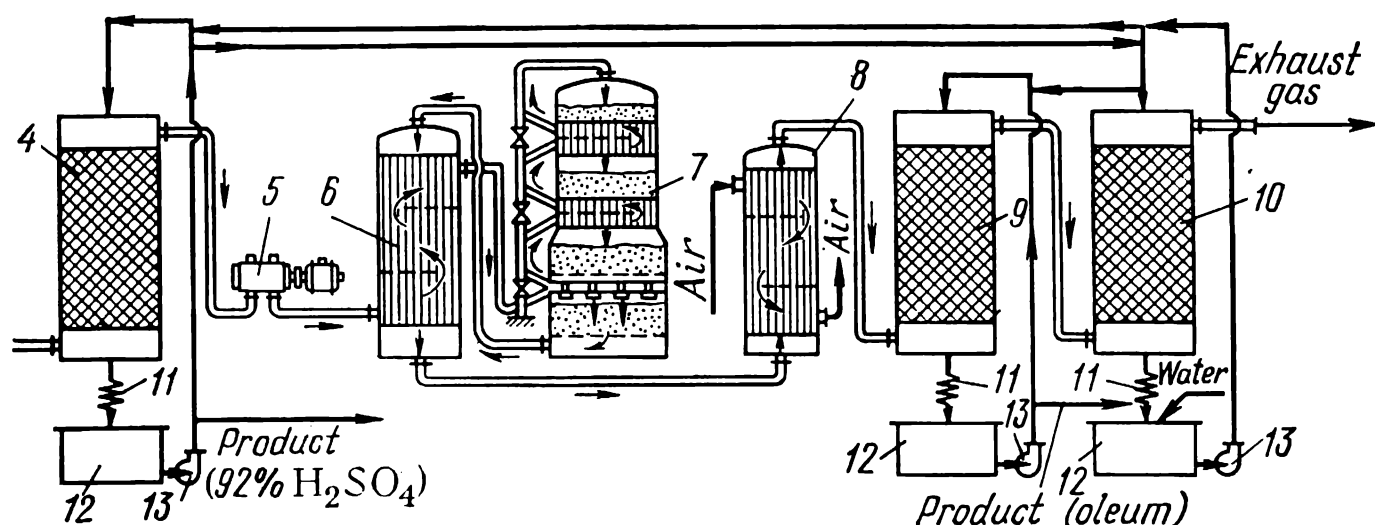


shelf-type apparatus in which the temperature is lowered between shelves by introducing cold air is also used. Best heat removal and maximum catalyst activity are achieved in reactors with four or five fluidized catalyst beds (see Part I, Fig. 114) and with coolers located within the beds of the catalyst.

Due to disintegration and sintering of the pellets, contamination of the bed, poisoning of the catalyst by arsenic compounds and mechanical damage by high temperatures during deviations from normal operating conditions the vanadium catalyst must be replaced on the average once every four years. However, if the gas-purification plant goes out of order, operation of the catalytic reactor is disrupted within a few days by poisoning of the first layer of the catalyst. To maintain high catalyst activity wet gas-purifying processes, which afford a high degree of purification, are used.

A flow diagram of a plant for manufacturing sulphuric acid by a contact process is given in Fig. 7.

The roaster gas, after preliminary separation of dust in pyrite-cinder electrostatic filters, at a temperature of about 300 °C is fed to a spray-type scrubber to which cold sulphuric acid (concentration about 75%) is introduced at the top. When the gas is cooled the sulphur trioxide and water vapour contained condense into tiny drops in which arsenic oxide dissolves. An arsenic-acid mist is formed which is partially separated from the gas in the first and second towers, which contain a ceramic packing. Simultaneously, remaining dust, selenium and other impurities are also removed. Sulphuric acid, containing impurities (up to 8% of the total output), is formed which is removed as a below-standard product. Final separation of the difficult-to-remove arsenic acid mist is carried out in wet electrostatic filters, used in groups of 2 or 3 consecutive units. The operating principle of wet electrostatic filters is the same as for dry ones. The drops of the mist settle on tubular precipitating electrodes made of lead or a special kind of plastic, and flow down along them. Gas purification is completed by drying the gas with vitriol oil in a packed tower. There are usually two consecu-



tive drying towers. The towers, pipes and acid vats in the gas purification section are most often made of steel with an acid-resistant lining of brick or diabase tile. Dry  $\text{SO}_2$  and  $\text{SO}_3$  are not corrosive, and, therefore, all the subsequent apparatus, up to the monohydrate absorber, can be made of ordinary carbon steel, not protected against corrosion.

The large number of units in the process chain results in considerable resistance to gas flow (up to 2 m of water column), and because of this a turbocompressor is necessary for moving the gas through the system. The compressor draws the gas from the roasters and through the apparatus which follows and then pushes it through the reactor unit.

The reactor unit usually consists of a reactor, heat exchangers of the tube-and-shell type and a furnace-type start-up gas heater not shown in Fig. 7. During starting up operations, and also if the temperature in the apparatus should drop below the desired value, the temperature of the gas on its way to the catalytic reactor is raised in the heater.

Ordinarily, shelf-type reactor units are used (see Part I, Fig. 105). A unit of this type has a cylindrical outer shell from 3 to 12 m in diameter and 10 to 25 m high. There are four or five gratings inside the shell, each of which carries a bed of the catalyst granules, and intermediate tube- or box-type heat exchangers between the catalyst beds. The fresh gas is heated by interchange with the hot gas from the reactor, at first in an external heat exchanger and then part or all of it is passed consecutively through three or four internal heat exchangers, and at 440–450 °C the gas is introduced into the first catalyst bed. The temperature is controlled by means of gate valves in the by-pass line. The internal heat exchangers are mainly necessary for cooling the gas after its partial oxidation and a rise in the temperature due to the heat of the reaction—in such a way as to stepwise approximate the optimal-temperature curve (see Part I, Fig. 104).

Operating conditions for a five-shelf apparatus with intermediate heat exchangers at concentrations of the inlet gas of 7%  $\text{SO}_2$  and 11%  $\text{O}_2$  are given in the diagram of Fig. 8. The equilibrium curve 1 was computed using equations (1.4)-(1.7). The optimal-temperature curve 2 which corresponds to a maximum process rate, can be computed using equation (6.16) (see Part I). For vanadium catalysts, with

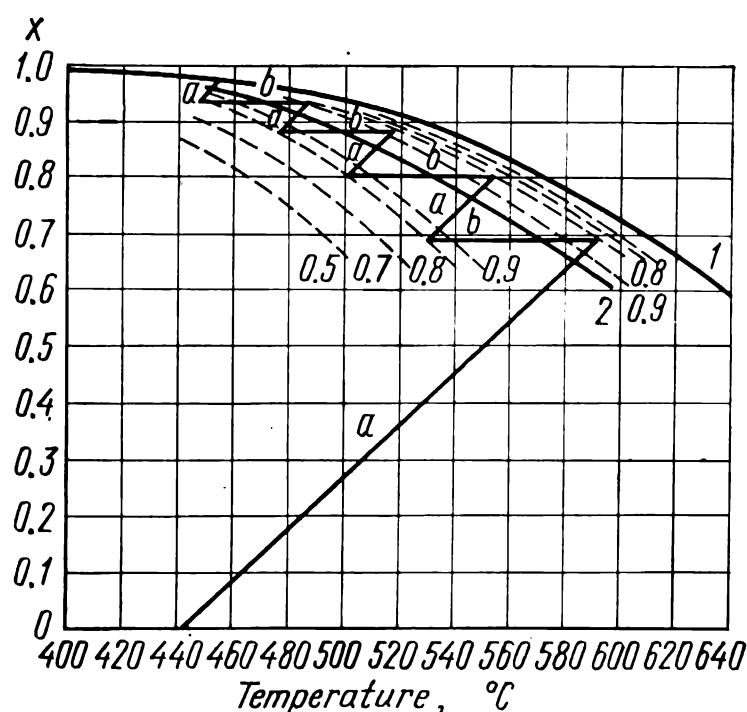


Fig. 8. The  $x$ - $t$  diagram for a five-bed apparatus with intermediate cooling:  
1—equilibrium curve; 2—optimal-temperature curve;  $a$ —adiabates of processes in the catalyst beds;  $b$ —gas-cooling process lines in the heat exchangers

an activation energy value of  $E = 90.0$  kJ/g-mole  $\text{SO}_3$ , and a kinetics-limited process, the optimal temperature ( $^{\circ}\text{K}$ ) is calculated using the equation

$$T_{\text{opt}} = \frac{4905}{\log \frac{x}{(1-x) \sqrt{\frac{C_{\text{O}_2} - 0.5C_{\text{SO}_2}x}{100 - 0.5C_{\text{SO}_2}x}}} + 4.937} \quad (1.17)$$

where  $4905 = \frac{2.3R}{Q_r}$ ;  $Q_r$  is the heat of the reaction, whose value at the catalyst ignition temperature can be computed using the approximate equation

$$Q_r = 101\,400 - 9.26T \text{ J/mole } (24\,205 - 20.21T \text{ cal/mole}) \quad (1.18)$$

The dashed curves of Fig. 8 correspond to reaction rates of 0.9, 0.8, 0.7 and 0.5 of the maximum values (on the optimal-temperature curve). The adiabatic curves  $a$  were computed using equation (6.13), and lines  $b$ —from the heat balance of the heat exchangers (see Part I).

As can be seen from Fig. 8, for a five-shelf apparatus at 7%  $\text{SO}_2$  in the inlet gas, four catalyst beds can operate at reaction rates above 0.8 of the maximum values and only the first bed operates at an unfavourable temperature. However, in the first bed the rate of the reaction is exceedingly high due to the high concentrations of the reactants and therefore the amount of catalyst in the bed is small. Decreasing the number of catalyst beds would result in a large deviation from the optimal-temperature curve and in reduced final conversion, whereas increasing the number of catalyst beds would complicate the design of the converter. Five beds are considered to be the optimum number.

The capacity of catalytic reactors, depending on their size, varies from 50 to 1000 tons per 24 hours, in units of 100 per cent  $\text{H}_2\text{SO}_4$ ; 200-300 litres of catalyst per ton  $\text{H}_2\text{SO}_4$  per 24 hours are loaded into the unit.

Tubular contacting apparatus (see Part I, Figs. 108 and 109) are used for oxidizing the  $\text{SO}_2$  less often than shelf-type units.

Fig. 9 shows a modern catalytic reactor with external heat exchangers; its production capacity is 1000 tons  $\text{H}_2\text{SO}_4$  per 24 hrs. The reactor is 12 m in diameter and it has an overall height of 22 m. Calculations for catalytic reactors with a stationary catalyst bed can be carried out with sufficient accuracy for practical purposes using a model of adiabatic ideal plug flow.

For oxidizing  $\text{SO}_2$ -containing gases with high concentrations of  $\text{SO}_2$ , fluidized-bed reactors (see Part I, Fig. 114) can be utilized with advantage.

To reduce the  $\text{SO}_2$  content of the stack gas a double-contacting procedure is widely used, by which the oxidation of  $\text{SO}_2$  over a catalyst is carried out in two stages. In the first stage the degree of conversion is about 0.90. Prior to the second stage of contacting  $\text{SO}_3$  is removed from the gas; this results in a shift in the equilibrium and raises the degree of conversion at equilibrium ( $x_e$ ). Due to this in one or two beds of the catalyst of the second stage of reaction the degree of conversion of sulphur dioxide reaches 0.95-0.97. The overall degree of conversion is 0.995-0.997, and the

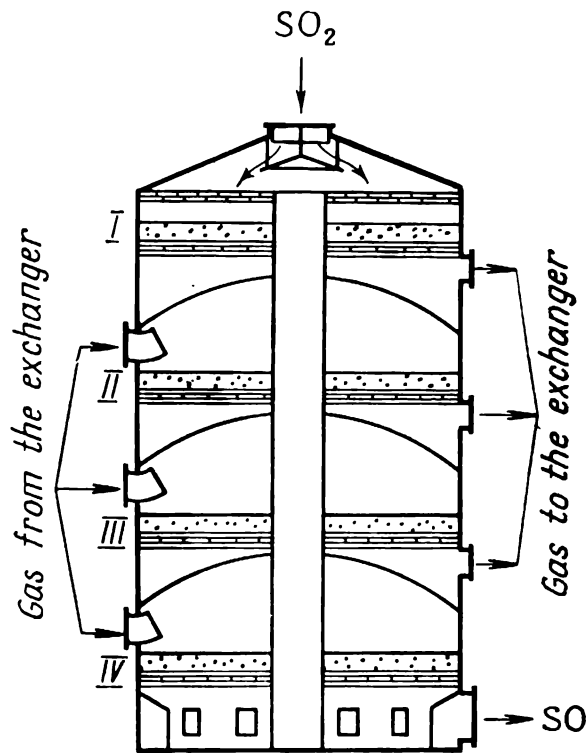


Fig. 9. A contacting apparatus with external heat exchangers:

I-IV - beds of the catalyst



SO<sub>2</sub> content of the stack gas is reduced to 0.003%. In the double-contacting procedure the gas is heated from 50 °C to 420-440 °C twice—prior to the first and then second stage of contacting, and therefore the initial sulphur dioxide concentration must be higher, than for single-stage conversion, in accordance with the adiabatic reaction equation [see Part I, (3.90)].

Fig. 10 is a flow diagram of a reactor section with double contacting. The gas passes through exchangers 1 and 2 and then, successively, enters the first, second and third bed of catalyst of reactor 3.

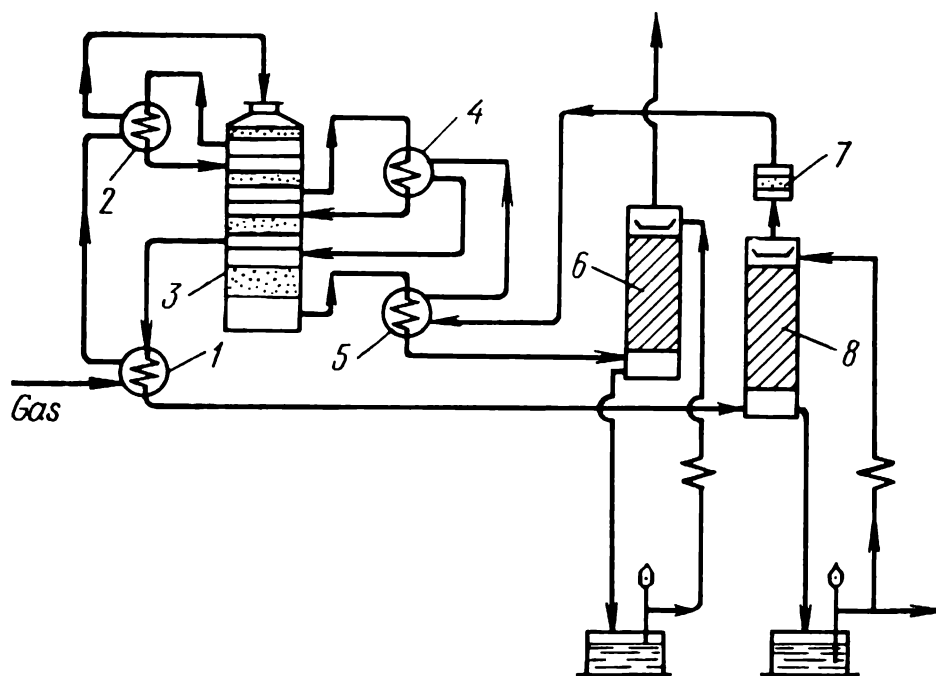
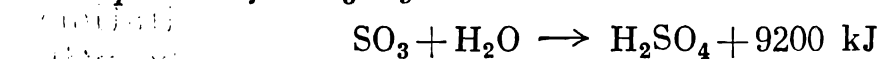


Fig. 10. A reactor section with double contacting:

1, 2, 4, 5—heat exchangers; 3—catalytic reactor; 6, 8—absorbers; 7—fibre filter

Upon leaving the third bed the gas goes to the intermediate absorber 8, from it to exchangers 5 and 4 and then to the fourth catalyst bed. The gas cooled in exchanger 5 flows through absorber 6 and is then discharged to the atmosphere.

*Absorption of SO<sub>3</sub> by the reaction:*



is usually carried out in packed towers, since tray-type absorbers with higher operating intensity offer larger resistance to gas flow. If the H<sub>2</sub>O-vapour pressure over the absorbing acid is high, SO<sub>3</sub> unites with H<sub>2</sub>O in the gas phase to form tiny particles of difficult-to-remove sulphuric-acid mist. Because of this, concentrated acids are used for absorbing SO<sub>3</sub>. The best acid strength is 98.3% H<sub>2</sub>SO<sub>4</sub>; such acid has extremely low partial pressures both of water vapour and of SO<sub>3</sub>. However, the concentration of the acid cannot be raised from 98.3% to that of standard oleum, 18.5-20% SO<sub>3</sub>, by one passage through the tower. Due to the large heat of absorption, if the

process in the tower is adiabatic, the acid temperature rises and absorption ends. Therefore, for producing oleum, absorption is carried out in two consecutive packed towers; oleum is fed to the first and 98.3% acid to the second. To improve absorption both the gas and the acid entering the absorber must be cooled as this increases the driving force.

In all the towers of the system, including the absorbers, the volume of liquid fed to a tower is many times larger than is theoretically necessary for absorbing the components of the gas mixture ( $\text{H}_2\text{O}$ ,  $\text{SO}_3$ ), and it is determined by the heat balance. For cooling the circulating acid drip coolers are usually used, in which the acid flows through tubes cooled from the outside with cold water.

The manufacture of contact sulphuric acid is a large-scale, continuous, mechanized process. Integral control of contact sulphuric acid plants is now being introduced. Consumption coefficients for sulphuric-acid production from pyrites, referred to one ton of monohydrate ( $\text{H}_2\text{SO}_4$ ) produced, comprise approximately: 0.82 t standard (45% S) pyrite; 82 kWh of electric power, and 50  $\text{m}^3$  of water. The cost of the pyrite contributes about 50% on the average of that of the acid. The level of mechanization is so high that wages add only about 5% to the cost of the acid.

If fluidized-bed reactors are used it is rational to produce and convert a gas containing 11-12%  $\text{SO}_2$  and 10-9%  $\text{O}_2$  since this results in a sharp decrease in the size of the apparatus and gives savings in electric power for operating turbocompressors and pumps.

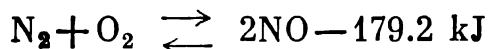
The most important features of new developments in the manufacture of sulphuric acid are typical of developments in many industrial chemical production processes. (1) Increasing unit production capacity of apparatus and introduction of integral control systems. (2) Intensifying production processes by employing fluidized-bed reactors (furnaces and fluidized-bed catalytic reactors) and high-activity catalysts; producing and converting sulphur dioxide using oxygen. (3) Developing power-and-technology flow schemes which provide maximum utilization of the heat of exothermic reactions, for instance recycle schemes and processes at high pressures. (4) Raising the degree of conversion in all stages of the production process to lower consumption of raw materials and reduce discharge of harmful effluents to the atmosphere. (5) Utilization of sulphur compounds ( $\text{S}$ ,  $\text{SO}_2$ ,  $\text{SO}_3$ ,  $\text{H}_2\text{S}$ ) contained in technological flow streams and stack gases, and also in the liquid effluents of other manufacturing processes. (6) Decontamination of gaseous and liquid effluents.

### 1. Combined Nitrogen and Its Importance for Human Life. Methods for Combining Atmospheric Nitrogen

Nitrogen belongs to that group of the chemical elements which play an extremely important part in nature and human life. Nitrogen is a participant in the basic biochemical processes. As a component of proteins it is a part of the most important form of foodstuffs for men and animals. It is not however elemental nitrogen which takes part in the synthesis of proteins in plants, but combined nitrogen, i.e. its chemical compounds. Ammonia is employed in manufacturing nitric acid and nitrogenous fertilizers. In times of peace nitrogen compounds are mainly consumed for manufacturing fertilizers. Nitrogen compounds are also used in making intermediate products and dyes, plastics (for example aminoplastics), chemical fibres, photography chemicals, pharmaceuticals and a number of other products of commercial importance. Nitrogen compounds play a very important part in the manufacture of explosives and incendiaries.

There are very few natural sources of combined nitrogen which are of commercial importance. Large deposits of combined nitrogen in the form of sodium nitrate were discovered in Chile and, later, in South Africa. A certain amount of combined nitrogen (ammonium sulphate) is obtained from coke gas, however this is a relatively minor source. Nitrogen compounds were synthesized from the uncombined nitrogen of the atmosphere at the beginning of the 20th century by three methods—the arc, cyanamide and ammonia methods.

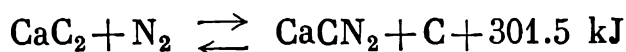
The arc method is based on the reaction of nitrogen with oxygen of the air at high temperatures



The nitrogen monoxide is oxidized to the dioxide, which is absorbed with water to produce  $\text{HNO}_3$ . This method was abandoned due to low yield of the monoxide and the tremendous energy consumption for the formation of the electric arc. However, at present, a similar method of high temperature oxidation of nitrogen by oxygen of the air is being resurrected based on the use of plasma procedures.

The cyanamide method is based on the reaction of nitrogen with finely crushed calcium carbide at a temperature of about  $1000^\circ\text{C}$

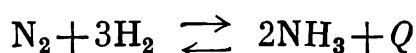
as described by the equation:



At present the share of this method in commercial production of combined nitrogen is small.

**The ammonia method** for combining atmospheric nitrogen is the most economically effective of the methods. Power consumption per ton combined nitrogen made by this method is considerably lower than for the electric-arc and cyanamide methods.

The first commercial ammonia-synthesis plant was built in Germany in 1913. Ammonia synthesis proceeds by the reaction:



The ratio of nitrogen to hydrogen (the nitrogen-hydrogen mixture) needed for the synthesis is  $\text{N}_2 : \text{H}_2 = 1 : 3$ . The nitrogen necessary for producing the nitrogen-hydrogen mixture is derived from the air by two, basically different, methods: (1) by physical separation of air into nitrogen and oxygen, and (2) by obtaining the nitrogen together with the necessary amount of hydrogen through combining all the oxygen of the air into  $\text{CO}_2$ , and then separating the  $\text{CO}_2$  from the hydrogen-nitrogen mixture. The hydrogen is obtained from methane, and its homologues, water gas, producer gas, coke-oven gas or water.

## 2. Producing Nitrogen and Oxygen by Separation of Air

The principal individual gases in the air are: nitrogen (78.03%), oxygen (20.95%), argon (0.94%) (volume per cent in dry air). Air also contains small amounts of  $\text{H}_2$ , Ne, He, Kr, Xe and  $\text{CO}_2$ . Some of the gases contained in the air are extensively used in a number of branches of industry.

Air is separated into its components by distillation, based on the difference in the boiling points of the individual gases in

TABLE 1  
Melting Points, Boiling Points and Critical Temperatures  
of  $\text{O}_2$ , Ar, and  $\text{N}_2$

Gas	Melting point, °C	Boiling point, °C	Critical points	
			tempera- ture, °C	pressure, atm
Oxygen ( $\text{O}_2$ )	−218.4	−182.95	−118.8	51.35
Argon (Ar)	−189.2	−185.7	−122.7	49.6
Nitrogen ( $\text{N}_2$ )	−209.9	−195.8	−147.8	34.6

liquefied air. The most complex stage in the process is the conversion of the air to the liquid state.

Table 1 lists some of the physical properties of air components.

It is evident from these data that air can be converted to the liquid state\* by a combination of low temperature and high pressure.

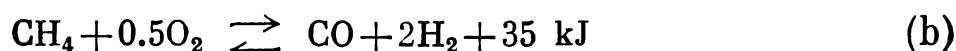
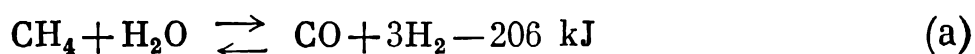
### 3. The Manufacture of Hydrogen and of the Nitrogen-Hydrogen Mixture for Ammonia Synthesis

The hydrogen required for commercial ammonia synthesis can be obtained by one of the following methods:

(1) reforming of methane in natural gas, or its homologues, followed by conversion of the CO formed; (2) conversion of the carbon monoxide in water gas or semiwater gas, obtained by gasifying solid or liquid fuels; (3) separation of coke-oven gas by liquefying in succession all the components of the gas mixture, except hydrogen; (4) electrolysis of water and sodium-chloride solutions.

At present solid fuel has practically almost completely been replaced by gaseous raw materials: natural gas, casing-head gas, petroleum-processing gases and the gas remainder of the process for making acetylene from natural gas.

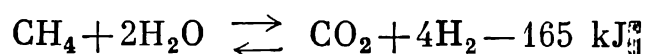
**Producing hydrogen by methane reforming.** Methane reacts with steam and oxygen in the following principal ways



The reactions of methane homologues with these oxidizing agents take place in a similar fashion. The carbon monoxide produced reacts with steam according to:



The overall process of methane reforming with steam involves heat consumption



Methane reforming to CO and H<sub>2</sub> is carried out both at close-to-atmospheric and at high pressures over a catalyst (catalytic reforming) or without one (high-temperature methane reforming).

For the ammonia-synthesis process a nitrogen-hydrogen mixture containing no more than 0.5% CH<sub>4</sub> is necessary to prevent large gas losses with the purge in the ammonia-synthesis section. The methane remainder depends on the process temperature and also on the vapour : gas ratio and the pressure employed (see Tables 2 and 3).

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\* Air liquefaction and separation methods are studied in *Unit Processes* and *Unit Operation* courses.

TABLE 2

**The Equilibrium Composition of the Steam-Gas Mixture in Methane Reforming with Water Vapour at Atmospheric Pressure**

Temperature, °C	CH <sub>4</sub> : H <sub>2</sub> O ratio = 1 : 1 vol. %				CH <sub>4</sub> : H <sub>2</sub> O ratio = 1 : 2 vol. %				
	CO	H <sub>2</sub>	CH <sub>4</sub>	H <sub>2</sub> O	CO	H <sub>2</sub>	CH <sub>4</sub>	H <sub>2</sub> O	CO <sub>2</sub>
600	15.8	47.0	18.6	18.6	6.95	53.28	8.25	23.42	8.10
700	21.5	64.5	7.0	7.0	13.37	62.76	1.61	16.59	5.67
800	23.8	71.6	2.3	2.3	15.67	63.93	0.17	16.00	4.23
900	24.6	73.8	0.8	0.8	16.59	63.36	0.02	16.63	3.40

TABLE 3

**The Equilibrium Methane Remainder as a Function of the Pressure and Temperature, CH<sub>4</sub>: H<sub>2</sub>O = 1 : 2**

Pressure, atm <sup>2</sup>	Process temperature necessary (°C) at methane content of equilibrium mixture, expressed in vol. %				
	5.0	2.0	1.0	0.5	0.2
1	—	700	—	—	800
10	800	870	910	950	~ 1000
20 <sup>6</sup>	870	950	1000	1030	1100
40	940	1020	1080	1130	1200

At temperatures of 800-1000 °C the equilibrium methane content is already sufficiently small, however the rate of methane conversion without a catalyst is very low in this temperature range. Nickel deposited on aluminium oxide or on magnesium oxide is employed as a catalyst for the process. However, in spite of the fact that the methane content in the equilibrium mixture grows with pressure, the reforming process can be carried out with advantage at high pressures, used to increase the process rate. In this case the pressure of the gas delivered to the plant is utilized, which significantly lowers energy consumption for compressing the gas in the ammonia-synthesis process. At high pressures the volume of the apparatus and piping is less.

According to the nature of the oxidizing agent catalytic methane reforming methods are divided into steam-oxygen, carried out in one stage in shaft converters, and no-oxygen processes, carried out in two stages: first in a tubular catalytic reformer and then in a shaft converter. In steam-oxygen reforming of methane the heat consumed in endothermic reaction (a) is supplied by carrying out in the shaft

converter the exothermic reaction of oxidizing methane with oxygen (b). A mixture of natural gas, steam and enriched air (40-50%  $O_2$ ), produced in air separation units, is fed to the shaft converter. The temperature in the upper layers of the catalyst is kept within the limits 1050-1100 °C, and at the exit from the converter—at 800-900 °C.

In producing synthesis gas by no-oxygen catalytic reforming of natural gas a tubular converter is used with the catalyst in the tubes,

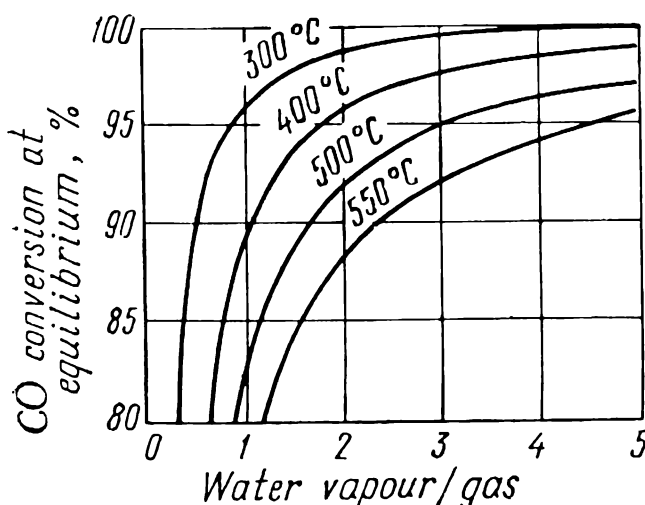


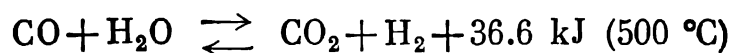
Fig. 11. Equilibrium carbon-monoxide conversion as a function of the water vapour/gas ratio and temperature

and the heat consumed is supplied by burning natural gas in the intertube space of the converter. The temperature in the zone of reaction is kept about 800 °C. The process is carried out so that the content of  $CH_4$  remaining in the gas leaving the tubular catalytic reformer is from 8 to 10%. The methane remainder is converted in a shaft converter by oxygen from air to produce a nitrogen-hydrogen mixture with a  $N_2 : H_2$  ratio of 1 : 3. In this case it becomes unnecessary to construct at the plant costly, with high energy consumption, air separation

units, and this results in markedly improved cost indexes of the process. High temperature noncatalytic methane conversion is carried out by reaction (b) at a temperature of about 1250 °C. The gas obtained in this way contains carbon black which is separated from it by scrubbing with hot water under pressure.

Gasification of solid and liquid fuels is also employed to produce synthesis gas containing  $CO$ ,  $H_2$ ,  $CO_2$  and  $N_2$ .

**Converting the carbon monoxide.** The gas obtained by reforming methane and producer gas (water- or semiwater gas) contain from 20 to 40% carbon monoxide. The reaction of  $CO$  with water vapour is reversible and exothermic



Inasmuch as there is no change in the volume of the gas as a result of the conversion of  $CO$ , raising the pressure will only increase the process rate and will have no effect on the equilibrium yield of the hydrogen. Increasing the content of water vapour in the gas mixture favours more complete  $CO$ -conversion (Fig. 11). Raising the temperature shifts the equilibrium of the reaction to the left, i.e. in the undesirable direction. However, at low temperatures the reaction rate is low, even over a catalyst.

Until recently iron oxide with oxides of chromium, aluminium, potassium and calcium added as promoters was employed as the catalyst for CO-conversion. With such catalysts it was possible to carry out the process at a sufficiently high rate only at temperatures of 450-500 °C, which gave a remainder of CO in the gas mixture of about 2-4%. Because of the high content of the CO-remainder complex and cumbersome ammoniacal-cuprous purification is necessary.

In recent years a low-temperature (zinc-chromium-copper) catalyst has been developed for CO-conversion with which it is possible to carry out the process at 200-300 °C and obtain a CO-remainder of between 0.2 and 0.4% CO. In this case catalytic purification is possible in which the remaining CO is hydrogenated to methane (methaning). However, the low-temperature catalyst is extremely sensitive to the presence of sulphur-containing compounds and this places special requirements on the gas-purification process.

In industry CO-conversion is carried out either at atmospheric or high pressure. For reversible exothermic processes, to which class conversion of CO belongs, the optimal temperature drops as the degree of conversion of CO to CO<sub>2</sub> grows. However, actually the temperature in the catalysis zone will increase, if heat is not removed. To resolve this conflict the conversion process is carried out in two stages, in a shelf-type converter, with the temperature of the gas lowered between the shelves by evaporating water.

**Purification of the gas.** In catalytic processes for producing ammonia the requirements with respect to the purity of the gas going to the catalyst are very strict. Thus, in natural gas being fed to the catalyst for methane reforming the sulphur content must not exceed 2 milligrams per cu m; the low temperature catalyst for CO conversion is very sensitive to the presence of sulphur-containing compounds. The activity of the ammonia synthesis catalyst is lowered by the presence of even traces of oxygen-containing or sulphur-containing compounds. Natural gas, however, contains, as a rule, a certain amount of sulphur compounds, typical of a given field, or added as an odorant. Gas leaving the CO converter contains large amounts of CO<sub>2</sub> (up to 30%) and also CO (from 0.5 to 4.0%). A high degree of removal of these impurities at minimum costs is one of the most difficult problems to solve in developing the technology of ammonia synthesis.

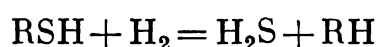
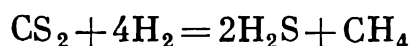
Various methods are used commercially for purifying the converted gas: (1) adsorption of impurities on solid sorbents; (2) absorption with liquid sorbents; (3) condensation of impurities at very low temperatures; (4) catalytic hydrogenation.

Solid sorbents are only used for a gas with a very low content of impurities (sulphur-containing compounds).

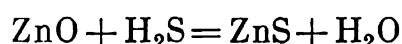


Purification with liquid sorbents in ammonia production is used for removing  $\text{CO}_2$  and  $\text{CO}$ . Purification by condensation at low temperatures is employed on a fairly broad scale at present in ammonia synthesis. However, this method does not find wide application, because of the increased electric power consumption, in the new schemas of ammonia production. Catalytic purification by hydrogenation and then removal of the water formed is used for small amounts of  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{O}_2$  in the converted gas.

**Removal of sulphur compounds.** Natural gas contains sulphur in the form of hydrogen sulphide, carbon bisulphide, carbon oxysulphide, mercaptans (mainly ethyl mercaptan,  $\text{C}_2\text{H}_5\text{SH}$ ), whose content varies from 5 to 30  $\text{mg/m}^3$ . Prior to the purification process the sulphur-oxygen compounds are converted to hydrogen sulphide by hydrogenation over a cobalt molybdenum catalyst at 350-450 °C at a space velocity of about 1000  $\text{hr}^{-1}$ . The reactions are:



The hydrogen sulphide formed is either adsorbed on solid sorbents or absorbed with liquids. Activated charcoal, ferrum hydroxide and zinc oxide are used as solid sorbents for removing hydrogen sulphide. Aqueous ammonia, ethanolamines, an arsenic-soda solution, solutions of carbonates, etc. are the liquids employed for absorption. In the combined nitrogen industry most frequent is purification using zinc oxide at a temperature of 350-400 °C and space velocity up to 2000  $\text{hr}^{-1}$  by the reaction

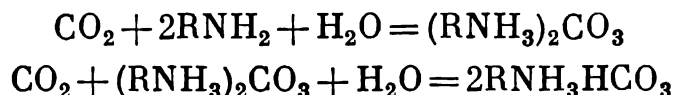


At 400-500 °C the reaction is practically irreversible. The sulphur capacity of the sorbent is about 30%. The content of  $\text{H}_2\text{S}$  at the exit from the sulphur purification unit does not exceed 1  $\text{mg/m}^3$ .

**Removal of  $\text{CO}_2$  from the converted gas.** After conversion of  $\text{CO}$  the gas contains from 17 to 30% of carbon dioxide, which is, usually, separated using liquid sorbents, such as water, ethanolamines, alkaline solutions, etc. Under pressure  $\text{CO}_2$  dissolves in water much better than the other components of the converter gas. This is the basis for using *water* to separate the  $\text{CO}_2$  by scrubbing the gas in packed towers under a pressure of 20-30 atm gauge. The water flowing out of the tower is fed to a turbine which is attached to the axle of the pump which delivers water to the top of the tower. This regenerates about 60% of the electric power consumed in pumping water to the tower. In the turbine the water pressure drops to the atmospheric level, the solubility of the gases is lowered and a mixture containing about 80%  $\text{CO}_2$ , 11%  $\text{H}_2$ , and also some  $\text{N}_2$ ,  $\text{H}_2\text{S}$ , and other gases is desorbed. This gas mixture can be employed with

advantage for manufacturing carbamide, dry ice or other products. The temperature of the water is lowered in cooling towers, after which it is recirculated to the scrubber. The most important negative features of purification with water are the high power consumption and large losses of hydrogen. Due to this in the most modern technological schemas other sorbents are used which have lower sorption capacities and higher selectivity than water.

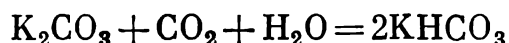
*Purification with ethanolamines* is carried out employing aqueous solutions of monoethanolamine,  $\text{CH}_2\text{CH}_2\text{OHNH}_2$ , and diethanolamine  $(\text{CH}_2\text{CH}_2\text{OH})_2\text{NH}$ . Separation of  $\text{CO}_2$  is based on the following reversible reactions:



where R denotes a  $(\text{OHCH}_2\text{CH}_2-)$  group.

Absorption is carried out at temperatures of 40-45 °C. The carbonates and bicarbonates formed in the process are decomposed in a desorber to release the  $\text{CO}_2$  by heating to 120 °C.

*Purification with a hot potash solution* is carried out under pressures of 10-20 atm at 110-120°. Usually a 25% aqueous solution of  $\text{K}_2\text{CO}_3$ , activated with arsenic ( $\text{As}_2\text{O}_3$ ) is employed. Upon dissolving  $\text{CO}_2$ , the carbonate is converted to the bicarbonate by the reaction



The solution is regenerated by lowering the pressure. Other possible solvents are methanol, propylene carbonate— $\text{C}_4\text{H}_6\text{O}_3$ , sulfolan— $\text{C}_4\text{H}_8\text{SO}_2$ .

**Removal of CO from the gas.** In an ammonia synthesis process CO is separated from the gas by one of the following methods: absorption in a cuprous-ammoniacal or acetate-carbonate solution, scrubbing the gas with liquid nitrogen, catalytic hydrogenation (at low CO-concentrations of the gas). Separation using a cuprous-ammoniacal solution is based on formation of a cuprous-ammoniacal complex compound with the carbon monoxide absorbed. The absorption capacity of cuprous-ammoniacal solutions under ordinary conditions is quite small, but when the pressure is raised and the temperature of the solution lowered absorption increases. This results in the use of high pressures (100-300 atm) and of temperatures, from 0° to 25 °C (crystallization from the solution may occur at lower temperatures), for removing CO from the gas. Usually cuprous-ammoniacal solutions of weak acids are employed—acetic (acetates), carbonic (carbonates) or formic (formates).

Regeneration of the solution is carried out at temperatures of 77-79 °C and atmospheric pressure; under these conditions the CO is desorbed. Regeneration of the cuprous-ammoniacal solutions can be carried out with advantage under vacuum. During regeneration

of the solutions part of the  $\text{NH}_3$  is lost and it must be replaced. The regenerated solution is cooled and then returned for CO-absorption. After CO-purification of the gas remaining CO does not exceed 0.003%.

**Condensation of admixtures at low temperatures.** Fractional condensation at low temperatures is used for the separation of coke-oven gas, which is a mixture of complex composition.

Table 4 gives a representative composition of coke-oven gas and the boiling points of the individual components of the gas mixture at a pressure of 760 mmHg.

TABLE 4  
Representative Composition of Coke-Oven Gas and the Boiling Points of Its Components

Component	Content, %	Boiling point, °C
$\text{H}_2$	54-59	−252.6
$\text{CH}_4$	23-28	−161.4
$\text{C}_2\text{H}_6$	2-3	−88.3
$\text{C}_2\text{H}_8$		−44.5
$\text{C}_3\text{H}_4$		−103.8
$\text{C}_3\text{H}_6$		−47.7
CO	5-7	−191.5
$\text{CO}_2$	1.5-2.5	−79.9
$\text{O}_2$	0.3-0.8	−183
$\text{N}_2$	about 5.0	−195.7

Table 4 shows that all the components of coke-oven gas except hydrogen have boiling points lying above  $-200^\circ\text{C}$  and that by deep cooling all the coke-oven gas constituents except hydrogen can be transformed to the liquid state.

For ammonia synthesis a nitrogen-hydrogen mixture is needed, and it is therefore not rational to remove the nitrogen contained in the coke-oven gas. Liquid fractions should, therefore, be separated from the gas down to the nitrogen boiling point,  $-195.7^\circ\text{C}$ . The

hydrogen obtained will also contain a certain amount of CO, which is a catalyst poison. In producing a nitrogen-hydrogen mixture from coke-oven gas it is, therefore, scrubbed with liquid nitrogen to remove the carbon monoxide remaining in it; in this process part of the nitrogen evaporates and the mixture approaches an  $N_2 : H_2$  ratio of 1 : 3. The mixture is brought up to the necessary  $N_2 : H_2$  volumetric ratio of 1 : 3 required for ammonia synthesis by adding nitrogen. Coke-oven gas separation is carried out under a pressure of 11-12 atm. In the coke-oven gas separation section the gas is first treated to remove hydrogen sulphide, carbon dioxide and water vapour. The separation unit consists of a number of heat exchangers, a scrubber tower, separators and throttling devices, all contained in a common shell.

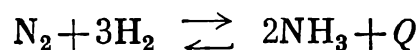
**Hydrogenation.** Methanation (hydrogenation) of small remainders of CO and  $CO_2$  (up to 1 %) proceeds according to the reaction equations



The process of methanation is carried out over nickel catalysts (on an aluminium oxide carrier) at 200-400 °C and at space velocities of 6 000 to 10 000 hr<sup>-1</sup>.

## 4. Ammonia Synthesis

**The theoretical basis of the ammonia synthesis process.** Ammonia synthesis takes place without formation of by-products by the reaction



The heat of the reaction of ammonia synthesis depends on the temperature and pressure and can be computed using the equation:

$$Q = 4.19 \left[ 9157 + \left( 0.545 + \frac{840.6}{T} + \frac{4597 \cdot 10^5}{T^3} \right) P + \right. \\ \left. + 5.35T + 2.52 \cdot 10^{-4}T^2 - 1.69 \cdot 10^{-6}T^3 \right] \text{ kJ/mole} \quad (2.1)$$

where  $T$  is the absolute temperature and  $P$  is the pressure in atmospheres.

Heat effects at a temperature of 500 °C and at different pressures computed from equation (2.1) are given below.

Pressure, atm	1	100	300	600	1000
$Q$ per mole $NH_3$ , kJ	50.2	52.0	55.8	61.4	68.8

The change in the equilibrium ammonia yield with pressure and temperature for a stoichiometric nitrogen-hydrogen mixture which does not contain impurities is given in Table 5.

TABLE 5

**Ammonia Content of the Gas Mixture at Equilibrium**

Temperature, °C	NH <sub>3</sub> -content (%) at pressure of	
	300 atm	1000 atm
200	89.94	98.29
300	70.96	92.55
400	47.00	79.82
500	26.44	57.47
600	13.77	31.43
700	7.28	12.83

As is evident from the table, high pressures and low temperatures must be employed to shift the equilibrium towards ammonia formation.

Ammonia synthesis proceeds at a very low rate even at high temperatures in the absence of a catalyst. Commercially, for obtaining the necessary reaction rate, ammonia synthesis is carried out at temperatures not lower than 400-500 °C and in the presence of solid catalysts. Many elements and various compounds of the elements have been tested as catalysts for this reaction. Iron, platinum, osmium, manganese, tungsten, uranium, rhodium and other metals with the next to the last electron shell of the atoms unfilled are catalysts for this reaction. Iron, osmium, rhenium and uranium exhibit the highest activity. For commercial synthesis of ammonia iron catalysts are used.

At present an iron catalyst which contains three promoters—Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, and CaO—is used extensively. It exhibits high activity combined with good resistance to overheating and to impurities in the nitrogen-hydrogen mixture.

Hydrogen sulphide and other sulphur compounds poison the iron catalyst irreversibly. For instance, presence in the catalyst of 0.1 % S reduces its activity twofold, and 1 % of sulphur completely poisons the catalyst. Oxygen and oxygen compounds (H<sub>2</sub>O, CO, CO<sub>2</sub>) exhibit a very pronounced poisoning effect, but it is reversible.

Ammonia synthesis is a typical heterogeneous catalytic process which consists of a number of stages:

1. Diffusion of nitrogen and hydrogen from the bulk of the gas to the surface of the catalyst granules and into the pores of the granules.

2. Activated (chemical) adsorption of the gases on the catalyst.

3. The reaction of nitrogen and hydrogen at the catalyst surface. Here, according to the electron theory, the nitrogen accepts electrons from the catalyst, and the hydrogen transfers electrons to the cata-

lysts, to make up for the electrons lost. This results in the successive formation of surface compounds: imide (NH), amide (NH<sub>2</sub>) and ammonia (NH<sub>3</sub>).

4. Desorption of the ammonia and its diffusion into the core of the gas phase.

The limiting stage of the process is that of activated nitrogen adsorption. The ammonia yield depends on many process variables: the temperature, pressure, time of contact of the gas with the catalyst (or the inverse value, called the space velocity), the composition of the gas mixture, catalyst activity and design of the apparatus. If the system variables are not far from equilibrium values the process rate can be approximated using the equation given by M. Temkin:

$$u = \frac{dp_{\text{NH}_3}}{d\tau} = k_1 p_{\text{N}_2} \cdot \frac{p_{\text{H}_2}^{1.5}}{p_{\text{NH}_3}} - k_2 \frac{p_{\text{NH}_3}}{p_{\text{H}_2}^{1.5}} \quad (2.2)$$

where  $k_1$  is the rate constant of ammonia synthesis;  $k_2$  the rate constant of ammonia decomposition;  $p$  the partial pressure.

The constants  $k_1$  and  $k_2$  are interrelated by  $\frac{k_1}{k_2} = K$ ,  $K$  being the equilibrium constant of the ammonia synthesis reaction. Usually the activity of the catalyst is characterized by a rate constant  $k$ , which is directly proportional to  $k_1$ . The value of the rate constant  $k$  depends on a number of factors: the temperature, catalyst activity, pellet size. At high pressures  $k$  becomes a function of the overall pressure. Ratios of the  $k$ -value at a pressure  $P$  to that at atmospheric pressure, denoted by  $k^0$ , are given below.

$P, \text{ atm}$	1	100	200	300	400	500
$\frac{k}{k^0}$	1	0.92	0.8	0.75	0.7	0.65

The ammonia content in the gas at the converter exit can be found from

$$k = P^{0.5} V_0 \int_{C_1}^{C_2} \frac{C(1-C) dC}{(1+C)^2 [L^2(1-C)^4 - C^2]} \quad (2.3)$$

where  $C$  is the molar fraction of the ammonia;  $k$  the rate constant,  $\text{atm}^{0.5} \cdot \text{hr}^{-1}$ ;  $V_0$  the space velocity expressed in terms of gas with zero ammonia content, which is interrelated with the space velocity at the entrance to the converter,  $V_1$ , and at the exit,  $V_2$ , by the equations:

$$V_0 = V_1(1 - C_1) = V_2(1 - C_2) \quad (2.4)$$

where  $C_1$  and  $C_2$  are the molar fractions of ammonia at the reactor entrance and exit, respectively;  $P$  the pressure in the reactor;

$$L = \frac{C_e}{(1 - C_e)^2} \quad (2.5)$$

$C_e$  being the molar fraction of ammonia in the equilibrium gas mixture.

For approximate calculations the following formula can be used

$$k = -\frac{1}{2} P^{0.5} V_0 (1-C)^{3.5} \ln \left[ 1 - \frac{C^2}{L^2 (1-C)^4} \right] \quad (2.6)$$

The dependence of the rate constant, determined using the Temkin equation, on the temperature follows the Arrhenius equation. The activation energy of the reaction over an industrial catalyst is approximately 165 kJ/mole.

Fig. 12 contains data which characterize the dependence of the ammonia yield on temperature and space velocity at a pressure of

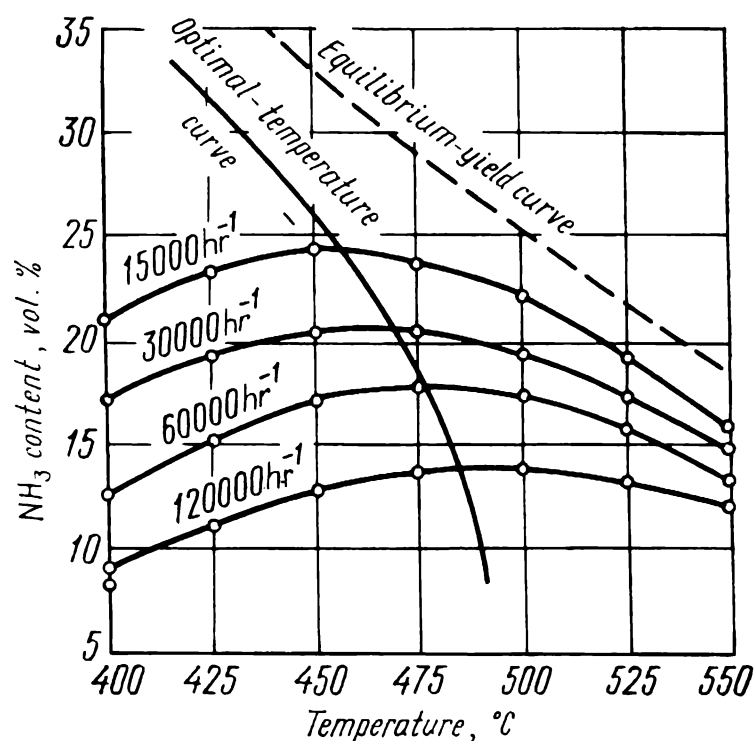


Fig. 12. Ammonia yield as a function of synthesis temperature and space velocity ( $P = 300$  atm)

300 atm for a stoichiometric nitrogen-hydrogen mixture. These data were obtained with an industrial iron catalyst. For approximate technological calculations the mean curve of the relationship between the ammonia content and the space velocity is used. The assumption is made that for a given pressure, given catalyst, and given gas composition the product yield does not depend on the temperature, because there are only small changes in it. Thus the product yield is a function of the residence time of the gas in the catalyst zone.

As can be seen from Fig. 13 under a pressure of 300 atm a sixfold increase of the space velocity (from 20 000 to 120 000 hr<sup>-1</sup>) results in a drop in the ammonia content of the gas mixture at the optimal

temperature (from 20 to 13%  $\text{NH}_3$ ) of only 1.5. Consequently, if the space velocity is increased, the yield of ammonia per cubic metre of catalyst rises sharply. However, this will be accompanied by a significant rise in the volume of unconverted nitrogen-hydrogen mixture, which will continuously circulate in the cycle. This results in increased energy consumption for transporting the gas, and increased size of pipes, heat exchangers and condensers. The selection

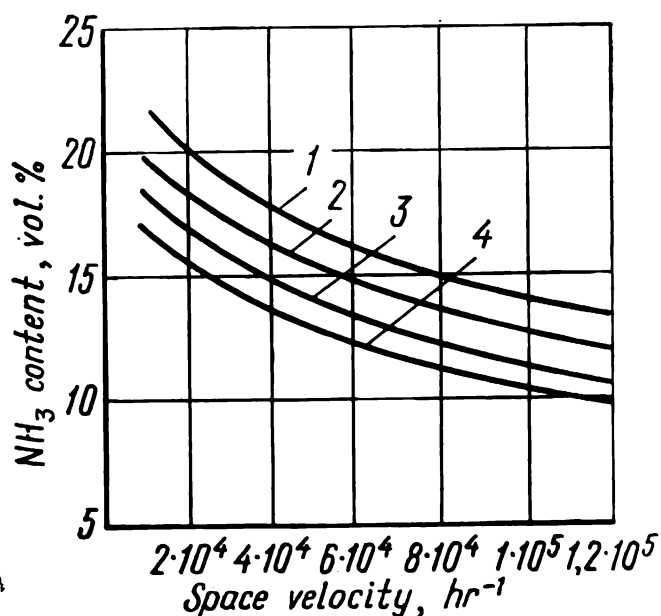


Fig. 13. Ammonia yield as a function of space velocity for different contents of chemically inert components of the recycle mixture at  $P = 300$  atm:

- 1— $\text{N}_2 + 3\text{H}_2$ , without chemically inert gases;
- 2— $\text{N}_2 + 3\text{H}_2 + 2\%$  chemically inert gases;
- 3— $\text{N}_2 + 3\text{H}_2 + 7\%$  chemically inert gases;
- 4— $\text{N}_2 + 3\text{H}_2 + 10\%$  chemically inert gases

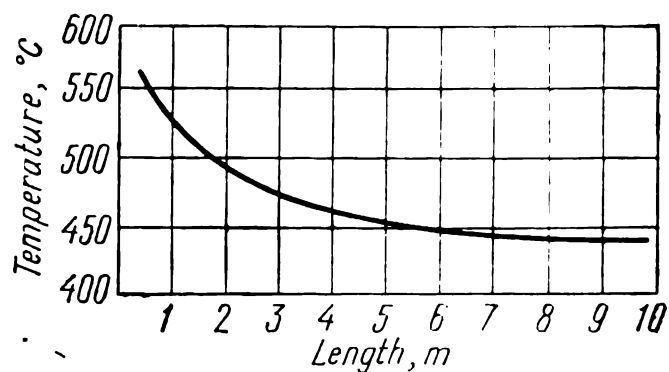


Fig. 14. Optimal temperature distribution along the length of the catalyst basket at a space velocity of  $15\,000\text{ hr}^{-1}$

of the optimal space velocity is, therefore, made on the basis of costs. At present ammonia-synthesis units operate with space velocities of  $15\,000$  to  $30\,000\text{ hr}^{-1}$ .

Fig. 13 is based on data regarding the mean yield of ammonia at  $450\text{--}525^\circ\text{C}$  at various contents of inert gases (methane and argon) in the circulating nitrogen-hydrogen mixture for a commercial catalyst.

Inasmuch as ammonia synthesis is a reversible exothermic process and the ammonia formed reduces the process rate, a decrease in the temperature along the length of the catalyst box will provide optimal conditions. Fig. 14 gives the optimal temperature distribution in the catalyst zone of a converter operating under a pressure of  $300\text{ atm}$ , with a space velocity of  $15\,000\text{ hr}^{-1}$  and approximately an 8% content of inert admixtures ( $\text{CH}_4$ , Ar, etc.) in the cycle.

The basic conditions for high productivity and stable operation of ammonia synthesis units are:



- (1) effective purification of the nitrogen-hydrogen mixture to remove catalyst poisons and inert admixtures;
- (2) maintaining the  $N_2 : H_2$  ratio close to 1 : 3;
- (3) optimal temperature conditions over the length of the catalyst zone;
- (4) a low ammonia content at the inlet to the catalytic reactor;
- (5) a well-designed converter (synthesis tower).

**Commercial ammonia-synthesis methods.** Pressures from 100 to 1000 atm are used in industrial ammonia-synthesis processes and, depending on the pressure, the systems are classified as low-pressure (100-150 atm), medium-pressure (250-600 atm) or high-pressure (600-1000 atm) ones. Systems operating at medium pressures are the most common, since the conditions favour separation of the ammonia and the rate of conversion is quite high.

The nitrogen-hydrogen mixture is not completely converted to ammonia in passing through the catalyst bed. The ammonia content of the gas leaving the converter lies between 14 and 20%. The gas mixture leaving the reactor is cooled, the ammonia condenses, is separated from the gas and the mixture of unreacted nitrogen and hydrogen is returned to the converter by a recycle compressor. Fresh nitrogen-hydrogen mixture is added to the circulating mixture in an amount corresponding to that of the ammonia formed in the converter.

In a recycle process the nitrogen-hydrogen mixture fed to the system must be of high purity. It is not possible in practice, however, to obtain an absolutely pure nitrogen-hydrogen mixture. In a recycle process even if the content of impurities ( $CH_4$ , Ar) is very low in the nitrogen-hydrogen mixture fresh feed, the admixtures gradually accumulate in the circulating gas and this lowers the capacity of the converter. To some extent the impurities dissolve in the condensed liquid ammonia and are removed from the cycle with it. However, the amount of impurities withdrawn with the product does not balance the amount introduced with the fresh nitrogen-hydrogen mixture, and in industrial plants part of the circulating gas mixture must be purged to the atmosphere to lower the content of impurities in the circulating gas.

In the USSR the most commonly used are units operating at medium pressures (300-320 atm). The flow diagram of such a unit is given in Fig. 15.

The nitrogen-hydrogen mixture, ready for synthesis, is fed to the top of the converter in which the ammonia synthesis reaction takes place. The nitrogen-hydrogen-ammonia gas mixture produced leaves the tower at a temperature of 400 °C, goes to a waste-heat boiler, then returns to the synthesis tower where it is passed through a heat exchanger and, at a temperature of 90-100 °C, through a water cooler and separator. At 300 atm only part of the ammonia is con-

densed in the water cooler. The turbine recycle compressor drives the gas through the condenser tower and evaporator, where the low temperature necessary for maximum separation of the ammonia from the gas mixture is created by evaporating liquid ammonia. From the condensation tower the gas returns to the converter. Usually

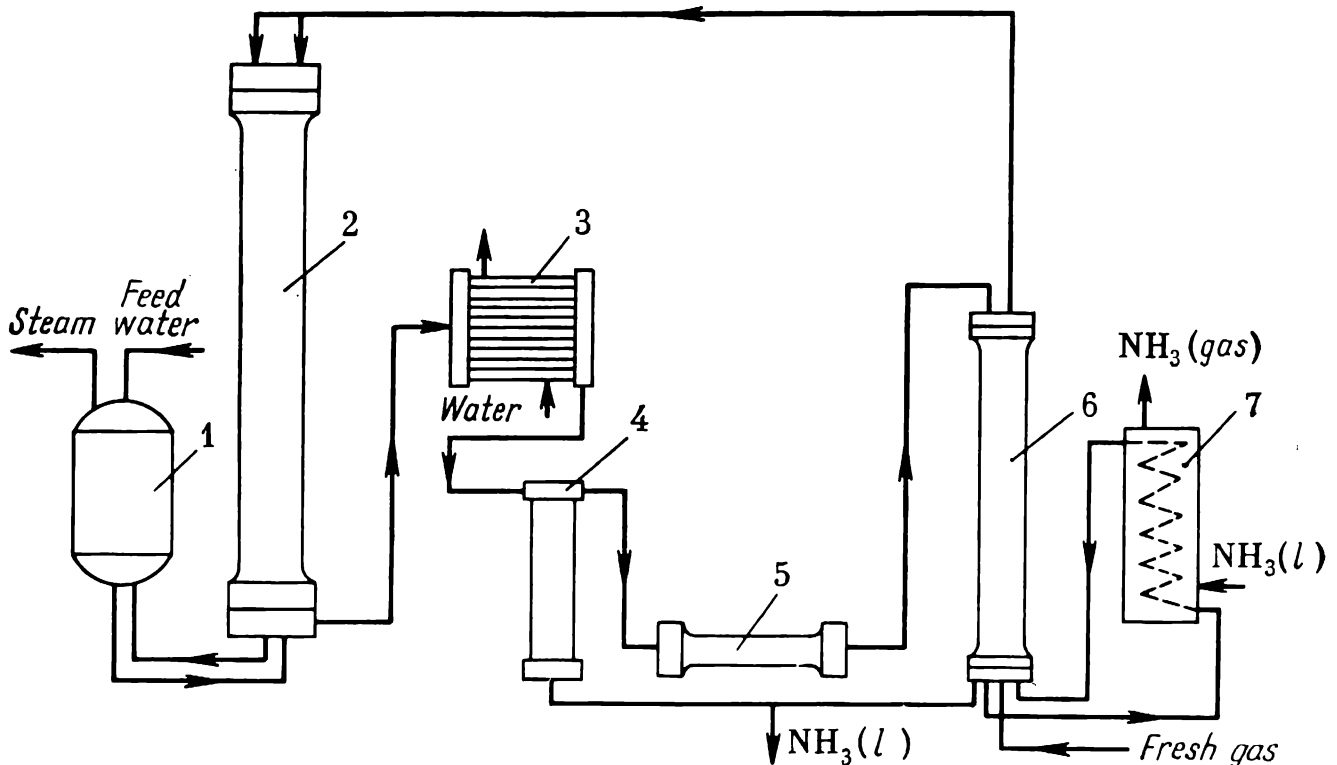


Fig. 15. Flow diagram of a unit for ammonia synthesis at medium pressure: 1—synthesis tower; 2—waste-heat boiler; 3—water cooler; 4—separator; 5—recycle compressor; 6—condensation tower; 7—evaporator

fresh nitrogen-hydrogen mixture is introduced at the bottom of the condensation tower, in which remaining water, oil and  $\text{CO}_2$  are removed by washing with liquid ammonia.

The relationship between the temperature and pressure and the ammonia content of the recycle nitrogen-hydrogen gas mixture over the liquid ammonia is shown in Fig. 16. It can also be computed using the empirical formula

$$\log C' = 4.1856 + \frac{5.9878}{P} - \frac{1099.5}{T} \quad (2.7)$$

where  $C'$  is the ammonia content of the nitrogen-hydrogen mixture, vol. %.

In drawing up the material balance of a synthesis unit per ton of ammonia produced, the following principal equations are employed.

Consumption of fresh gas,  $\text{m}^3$

$$V_{\text{fr}} = V_{\text{t}} + V_{\text{d}} + V_{\text{p}} \quad (2.8)$$

where  $V_t$  is the theoretical consumption of the nitrogen-hydrogen mixture, equal to  $2635 \text{ m}^3$ ;  $V_a$  the volume of gas dissolved in the liquid ammonia,  $\text{m}^3$ ;  $V_p$  the volume of the nitrogen-hydrogen mixture purged from the cycle together with the methane and argon removed,  $\text{m}^3$ .

The volume of the gas mixture at the converter inlet,  $\text{m}^3$ , is

$$V_1 = \frac{V}{g} \quad (2.9)$$

where  $V$  is the space velocity,  $\text{hr}^{-1}$ ;  $g$  catalyst productivity per ton  $\text{NH}_3$ ,  $\text{hr}^{-1} \cdot \text{m}^{-3}$ .

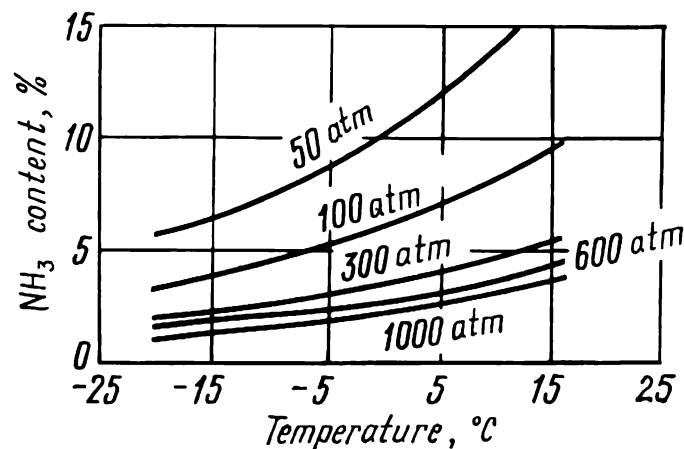


Fig. 16. Ammonia content of nitrogen-hydrogen mixture over liquid ammonia as a function of temperature and pressure

The capacity of the ammonia synthesis converter,  $\text{m}^3/\text{hr}$ , is

$$V_{\text{NH}_3} = V_1 \frac{C_2 - C_1}{100 + 1.03C_2} \quad (2.10)$$

$C_1$  being the ammonia content of the gas at the converter inlet, vol. %;  $C_2$  the ammonia content of the gas at the converter exit, vol. %.

The volume of the gas mixture leaving the converter is

$$V_2 = V_1 - V_t + V_{\text{NH}_3} \quad (2.11)$$

where  $V_{\text{NH}_3}$  is the volume of the ammonia formed in the converter,  $\text{m}^3$ .

The capacity of the water-cooled condenser is given by

$$V'_{\text{NH}_3} = V_2 \frac{C_2 - C_3}{100 - (1 + a_{\text{NH}} + a_{\text{m}} + a_{\text{Ar}}) C_3} \quad (2.12)$$

where  $V'_{\text{NH}_3}$  is the volume of gaseous ammonia which is condensed in the water-cooled condenser,  $\text{m}^3$ ;  $C_3$  the concentration of ammonia in the gas mixture leaving the condenser, vol. %;  $a_{\text{NH}}$ ,  $a_{\text{m}}$ ,  $a_{\text{Ar}}$

the solubilities of the nitrogen-hydrogen mixture, methane and argon, respectively (Fig. 17).

The volume of the gas leaving the preliminary separator,  $m^3$ , is

$$V_3 = V_2 - V'_{NH_3} - (a_{NH} + a_m + a_{Ar}) V'_{NH_3} \quad (2.13)$$

The capacity of the condensation tower,  $m^3/hr$ , is

$$V''_{NH_3} = V_{NH_3} - V'_{NH_3} - V_p C_3 0.01 \quad (2.14)$$

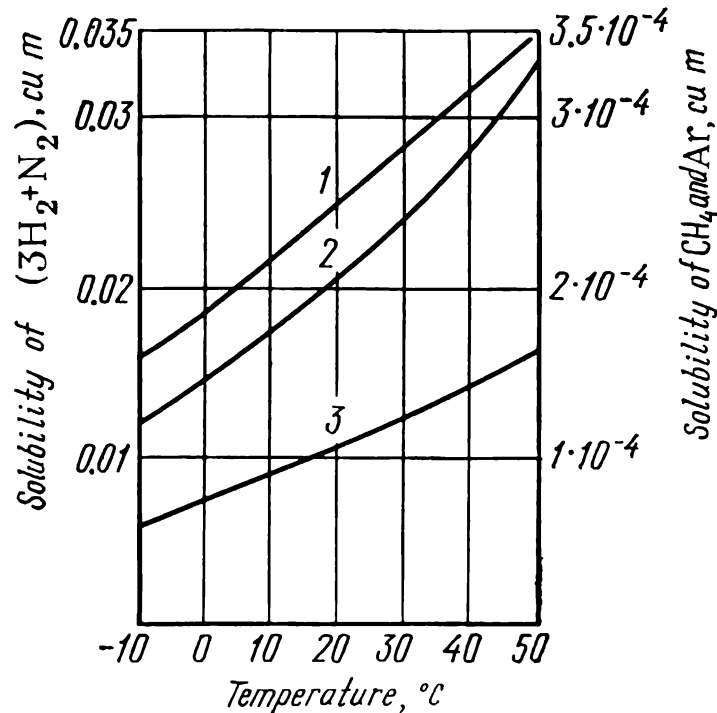


Fig. 17. Solubility of the nitrogen-hydrogen mixture, methane and argon in liquid ammonia, referred to 1 cu m gaseous  $NH_3$ :

1— $CH_4$ , at  $P = 1$  atm; 2— $N_2 + 3H_2$ , at  $P = 300$  atm; 3—Ar at  $P = 1$  atm

The volumes of the gases dissolved in the liquid ammonia,  $m^3$ , are

$$V_d = V_{NH} + V_m + V_{Ar} \quad (2.15)$$

$$V_{NH} = a_{NH} C_{NH} 0.01 (V'_{NH_3} + V''_{NH_3})$$

$$V_m = a_m C_m 0.01 (V'_{NH_3} + V''_{NH_3}) P$$

$$V_{Ar} = a_{Ar} C_{Ar} 0.01 (V'_{NH_3} + V''_{NH_3}) P$$

where  $C_{NH}$ ,  $C_m$ ,  $C_{Ar}$  are the contents of nitrogen-hydrogen mixture, methane and argon in the gas mixture, vol. %.

The total volume of the gas purged,  $m^3$ , is

$$V'_p = \frac{V_p}{1 - C_3} \quad (2.16)$$

The content of the inert impurities in the purge gas is determined from

$$V'_p = \frac{V_{fr} (C_m + C_{Ar}) 0.01 - V_m - V_{Ar}}{i} \quad (2.17)$$

$i$  being the content of the inert admixtures (methane and argon) in the recycle gas leaving the preliminary separator, vol. %. By using equation (2.17) the content of inert admixtures in the recycle gas can be determined for a given consumption of hydrogen-nitrogen mixture, or  $V_{fr}$  can be found for a given value of  $i$ .

The ammonia converter is the chief, most important, apparatus of a unit for manufacturing synthetic ammonia. The tower design

must be reliable and guarantee safe uninterrupted operation over long periods. The steel used for making the tower must, therefore, meet strict requirements.

The hydrogen and ammonia contained in the gas mixture interact with the steel at high temperatures, which results in deterioration of its strength. Especially dangerous is decarbonization of the steel at high temperatures by hydrogen, which penetrates into it. To lower the temperature of the tower walls the relatively cold nitrogen-hydrogen mixture entering into the converter is passed over the inner surface of the cylindrical tower wall. The body of the tower for synthesizing ammonia was formerly made from a chrome-vanadium steel casting by boring through it axially. It was then subjected to hammering and a complex process of thermal treatment and machining.

In recent years converter tower bodies made by bandaging or welding techniques have become common. The insides (packing) of the converter usually consists of a tubular catalytic reactor with

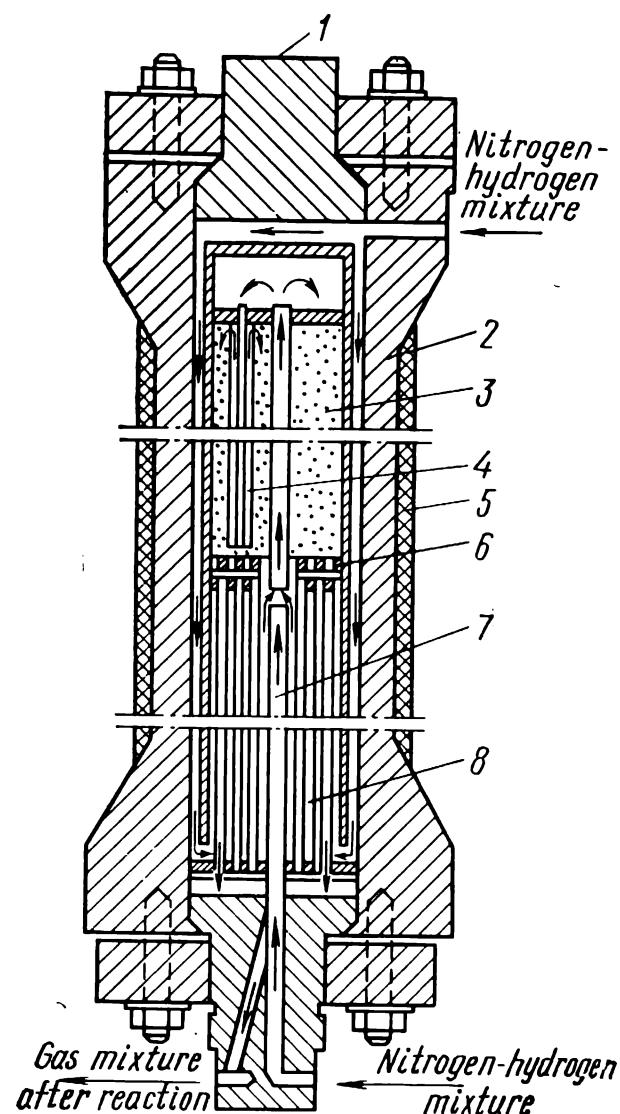


Fig. 18. Medium-pressure ammonia synthesis tower:

1—end covers; 2—tower shell; 3—catalyst basket; 4—heat exchanger; 5—heat insulation; 6—distribution plate; 7—central tube; 8—heat exchanger tubes

double heat-exchange tubes. Shelf-type reactors with axial flow of the gas through the layer of catalyst, and most recently, with radial flow are widely used.

Fig. 18 shows a tubular ammonia converter for operation at medium pressures. The tower consists of a steel cylinder 12-20 m high and with a wall 176-200 mm thick. The inner diameter of modern towers

is from 1.0 to 2.8 m. The tower is set up vertically. At the top and the bottom it has steel covers, joined to it by flanges.

Converters differ mainly in the size of the shell and the type of the inner packing. In the medium-pressure tower shown in the illustration there is a catalyst basket in the upper part and a heat exchanger, which provides an autothermal process, in the bottom part. The tower shell is covered with a layer of heat insulation, to protect against thermal stresses in the tower walls, which result from a large temperature difference of the inner and outer surfaces of the tower wall.

The catalyst rests on a grid. To achieve uniform temperature distribution throughout the catalyst bed there are numerous double tubes in the bed which serve as heat exchangers (see Part I, Fig. 112).

The nitrogen-hydrogen mixture enters into the ammonia converter at the top, passes down through the annular space between the tower shell and the catalyst basket to cool the apparatus wall and up through the intertube space of the heat exchanger. Then through the central tube it is delivered to the top of the catalyst basket and enters into the double tubes in the catalyst bed, first passing down through the narrow, inner tube from top to bottom and then up through the annular space between the narrow tube and the wider one. Further, the gas passes down through the catalyst bed, through the tubes of the heat exchanger and leaves the converter at the bottom. Gas flow through the catalyst bed is roughly of the plug-flow type and the temperature regime is a typical isothermal one.

To control the temperature in the converter tower cold nitrogen-hydrogen mixture can be directed through the central tube to the top of the catalyst basket by-passing the heat exchanger.

In converters of modern design the lower heat exchanger is divided into two parts so as to allow the heat of the reaction to be utilized: the gas leaving the catalyst basket passes through the upper part of the heat exchanger and at a temperature of 400 °C it goes to a waste-heat boiler, where it is cooled to 200 °C, and then returns to the converter, passes through the bottom part of the heat exchanger and is discharged from the converter at a temperature of 90-100 °C. External exchangers may also be employed.

The capacities of ammonia-synthesis towers now in use range from 150 to 1500 t of ammonia per day.

The capacity of an ammonia-synthesis converter can be calculated using the equation

$$G = \frac{V \cdot v (C_2 - C_1) 0.771}{100 + C_1} \quad (2.18)$$

where  $G$  is the converter capacity, kg/hr;  $V$  the space velocity,  $\text{m}^3/\text{m}^3 \times \text{hr}$ ;  $v$  the catalyst volume,  $\text{m}^3$ ;  $C_1$  the ammonia content of the hydrogen-nitrogen mixture entering the converter, %;  $C_2$  the ammo-

nia content at the converter exit, %; and 0.771 is the density of ammonia, kg/m<sup>3</sup>.

The capacity of an ammonia-synthesis column can be computed as illustrated in the following example for a column 14 m high and 850 mm in inner diameter, with 7% inert gases in the cycle, at a final ammonia condensation temperature of 5 °C, a space velocity of 25 000 hr<sup>-1</sup> and pressure of 300 atm.

Assuming that the utilization factor of the inner space of the ammonia-synthesis tower forged body is 35%, the volume of catalyst loaded into the synthesis column is found

$$V = 0.785d^2h \times 0.35 = 2.8 \text{ m}^3$$

From the data of Figs. 13 and 16 we find that in the initial period of column operation  $C_2 = 17\%$ ,  $C_1 = 4\%$ .

Then, by the formula

$$G = \frac{25\,000 \times 2.8 \cdot (17 - 4) \cdot 0.771}{104} = 6.7 \text{ t/hr or } 160 \text{ t per day}$$

After two years of operation the ammonia yield, due to a decrease in the catalyst activity, drops to 80% of the initial yield; it follows that

$$G = \frac{25\,000 \times 2.8 \cdot (13.5 - 4.0) \cdot 0.771}{104} = 4.9 \text{ t/hr} = 120 \text{ t per day}$$

Consequently the mean capacity of such a unit is 140 t NH<sub>3</sub> per day.

The life period of the catalyst depends on the efficiency of purification of the gas and at most plants it is approximately two years.

**Modern ammonia manufacturing schemas.** In developing new large capacity industrial units on the basis of the latest achievements in science and technology, the aim is to lower consumption of energy, materials and capital investments, and to attain a low cost product and high labour productivity. In the manufacture of ammonia this aim has been met by the creation of large units joined in a single flow stream with maximum utilization of both low potential and high potential excess heat.

High potential heat of gas-combustion products and the gases from converters is employed to produce high pressure steam which is used for driving turbines that power the compressors. Low potential heat is utilized in producing technologically employed low-pressure steam, hot water, refrigeration, etc. In the new systems air cooling is employed on a broad scale to reduce water consumption. Fig. 19 is a flow diagram of a 1500 tons per day system with two-stage steam-air methane reforming, high-temperature and low-temperature CO conversion, monoethanolamine removal of CO<sub>2</sub>, final purification from CO and CO<sub>2</sub> by catalytic hydrogenation (methanation) and ammonia synthesis.

Natural gas under a pressure of 40 atm, after removal of sulphur compounds from it, is mixed with steam to a ratio of 3.7: 1, heated in an exchanger by the effluent gases, and fed to a tubular furnace with a fire-box in which natural gas is burned. Over a nickel catalyst at 800-850°C methane is reformed with steam to produce carbon monoxide. The methane content of the gas following the first stage of conversion amounts to 9-10%. The gas is then mixed with air and flows through a shaft-type converter, where residual methane is

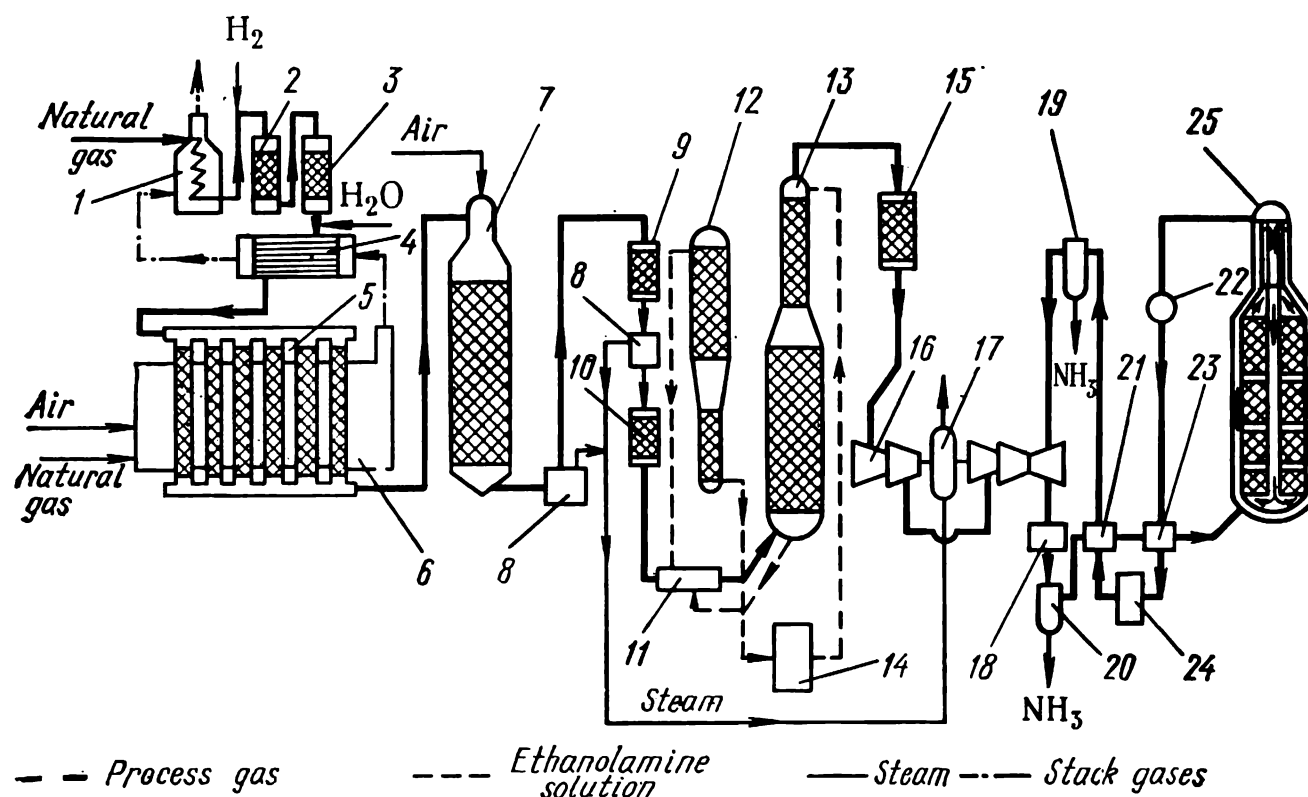


Fig. 19. Flow diagram of an ammonia synthesis unit:

1—natural gas heater; 2—reactor for hydrogenation of organic sulphur; 3—hydrogen-sulphide adsorber; 4—heat exchanger; 5—pipe furnace; 6—firebox; 7—checkbox methane converter; 8—boiler; 9—CO converter, 1<sup>st</sup> stage; 10—CO converter, 2<sup>nd</sup> stage; 11—heat exchanger; 12—CO<sub>2</sub> regenerator; 13—CO<sub>2</sub> absorber; 14—air cooler; 15—methanator; 16—turbocompressor with gas turbine; 17—steam turbine; 18—ammonia cooler; 19—primary separator; 20—secondary separator; 21—cold heat exchanger; 22—boiler-water heater; 23—"hot" exchanger; 24—air cooler; 25—tray-type reactor

converted to CO by the oxygen of the air at 900-1000 °C and a steam to gas ratio of 0.8 : 1. From the shaft-type converter the gas goes to a waste-heat boiler which produces high potential steam (100 atm, 480 °C) for use in the turbines of the centrifugal gas-compressors. Conversion of carbon monoxide is carried out in two stages, the first with a medium temperature iron-chromium catalyst at 430-470 °C, the second with a low temperature zinc-chromium catalyst at 200-260 °C. Between the two stages there is a waste-heat boiler. The heat of the gas mixture from the second stage of CO conversion is utilized for regenerating the monoethanolamine-solution effluent from the scrubber for removing CO<sub>2</sub> from the gas.



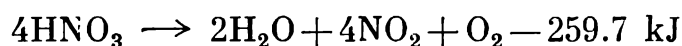
In this scrubber, to which cooled monoethanolamine solution at a temperature of 30-40 °C is fed at the top, CO<sub>2</sub> and CO are removed from the gas. At the exit from the absorber the gas contains a residue of oxygen-containing catalyst poisons (up to 0.3% CO and 30-40 cm<sup>3</sup>/m<sup>3</sup> CO<sub>2</sub>), which are hydrogenized at 280-350 °C over a nickel catalyst in the methanator. The excess heat of the purified gas leaving the methanator is utilized for heating the feed water; further cooling and separation of condensed water is carried out in an air cooler and a separator (not shown in the flow diagram). For compressing the nitrogen-hydrogen mixture to 300 atm and circulating the gas through the synthesis system a centrifugal compressor driven by a steam-condensation turbine was chosen. The last, recycler, impeller of the turbine is either located in a separate casing or combined with the fourth compression stage. Fresh nitrogen-hydrogen gas is added to the recycle gas upstream of the secondary condensation unit consisting of an ammonia cooler and separator; the gas mixture flows through two exchangers and into the synthesis tower. The gas, at a temperature of 320-380 °C, at the exit from the tower, passes through a heater for the feed water, the "hot" exchanger, an air cooler, the "cold" exchanger, a liquid-ammonia separator and goes to the recycler stage of the compressor. Liquified ammonia from the separators is delivered to the liquid-ammonia storage reservoir.

The most important development in the combined-nitrogen industry will be creation of units of great capacity (up to 3000 tons per day of NH<sub>3</sub> from a single line). An acute problem is that of developing new, high capacity, reactor designs, for example, with radial flow of the gas through the catalyst bed, which results in a sharp decrease in the pressure drop. Employing a fluidized bed of the catalyst is an interesting possible development. In a fluidized bed of the catalyst the interfacial area between the gas and the catalyst is increased sharply, and the synthesis-temperature conditions are improved, and this results in an intensified process.

The ammonia-synthesis process can be controlled automatically to provide optimal conditions and stabilize the process variables. All these developments lead to higher intensity of operation, to increased labour productivity and to better working conditions at ammonia-synthesis plants. Developing new, more active, low-temperature catalysts for ammonia synthesis, with higher resistance to poisoning and overheating is a matter of great importance.

### 1. General

Nitric acid is one of the most important of the mineral acids. Anhydrous nitric acid,  $\text{HNO}_3$ , is a heavy colourless liquid whose density at 15 °C is 1.52 and which fumes when exposed to air. It freezes at  $-41$  °C and boils at 86 °C. Boiling of the acid is accompanied by its partial decomposition, described by:



The nitrogen dioxide evolved dissolves in the acid and gives it a yellow or reddish colour, depending on the amount of  $\text{NO}_2$  present.

Nitric acid mixes with water in all proportions. The heat liberated when nitric acid is diluted with water is an indication of hydrate formation ( $\text{HNO}_3 \cdot \text{H}_2\text{O}$ ,  $\text{HNO}_3 \cdot 2\text{H}_2\text{O}$ ). When dilute nitric acid is evaporated, its content in the solution increases, up to a concentration of 68.4%  $\text{HNO}_3$ , which corresponds to an azeotropic mixture with a boiling point of 121.9 °C.

Nitric acid is a powerful oxidizing agent. All metals, with the exception of Pt, Rh, Ir and Au, are converted to the corresponding oxides by concentrated nitric acid. If the oxides are soluble in nitric acid, nitrates are formed. Iron is highly soluble in dilute nitric acid. High-strength acid forms a thin but dense layer of oxide, insoluble in such acid, on the surface of iron, which protects it from further corrosion. This surface-passivation property of iron is utilized to protect it against corrosion. Concentrated nitric acid (especially with an admixture of 10%  $\text{H}_2\text{SO}_4$ ) is usually transported in steel tanks.

Many organic substances (among them, animal and plant tissue) are destroyed by  $\text{HNO}_3$ , and some of them may ignite when brought into contact with high-strength acid. For laboratory use nitric acid containing about 65%  $\text{HNO}_3$  (density—1.4) is the common grade. There are two sorts of commercial nitric acid: dilute acid, with a 50-60%  $\text{HNO}_3$ -content, and concentrated acid, containing 96-98%  $\text{HNO}_3$ .

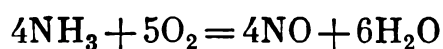
Up to the First World War nitric acid was manufactured almost entirely from saltpetre ( $\text{NaNO}_3$ ), large deposits of which were discovered in Chile at the beginning of the 19th century. At the beginning of the 20th century some amounts of nitric acid were produced

by the electric-arc method. However this process, which involves large electric-power consumption, did not come to be widely used (see also page 38). When processes for synthesizing ammonia were developed, the manufacture of nitric acid from ammonia spread all over the world.

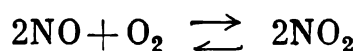
## 2. The Physical Chemistry of the Nitric-Acid Manufacturing Process

Production of dilute nitric acid from ammonia is based on the following reactions:

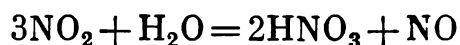
1. Catalytic oxidation of ammonia to nitric oxide:



2. Oxidation of nitric oxide to nitrogen peroxide:

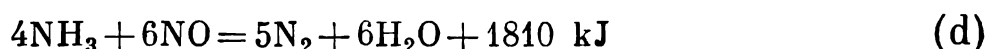
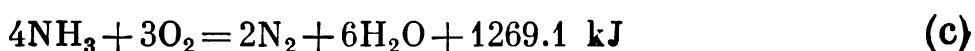
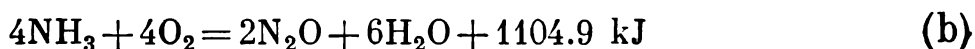
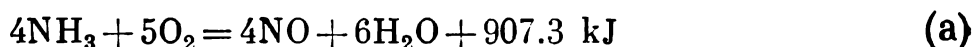


3. Absorption of nitrogen peroxide with water:



The nitric oxide liberated is reoxidized.

**Catalytic ammonia oxidation** is an exothermic process. Depending on the conditions, the following reactions between ammonia and oxygen are possible:



Reactions (a)-(d) are practically irreversible and the course of the overall process depends on the ratios of their reaction rates.

In the absence of a catalyst ammonia oxidation mainly results in formation of nitrogen by reaction (c). In manufacturing nitric acid maximum oxidation of ammonia by reaction (a) is desirable, and catalysts are used which selectively accelerate it. In industry the degree of oxidation of ammonia to nitric oxide with oxygen of the air reaches 98%.

Oxidation only proceeds at high temperatures; however, if the temperature is too high (above 900 °C) elemental nitrogen is formed.

Platinum and its alloys with metals of the platinum group, oxides of iron, manganese, cobalt and other substances can be employed as selective catalysts, which accelerate the rate of oxidation of ammonia to nitric oxide. Up to the present time, platinum and its alloys remain catalysts of unsurpassed activity for this reaction. Therefore, most plants for making nitric acid from ammonia use platinum catalysts. Non-platinum catalysts, which are cheaper, but less active,

are also widely used in the second stage of oxidizing ammonia to nitric oxide. Non-platinum (for example, iron-chromium) catalysts are employed in the form of pellets  $5 \times 4$  mm in size which are dumped into the reactor to form a 100-200 mm high layer.

Platinum catalysts are used in the form of wire gauze made of thin (0.06-0.09 mm diameter) wires with 1024 holes per square centimetre. The gauze is made of platinum-rhodium alloys (5-10% Rh), which are less subject to erosion during use and have a longer period of service than gauze made of pure platinum.

In recent years more active alloys which have 4% Pd and 3% Rh added to the platinum have come into use. The rate of ammonia oxidation to nitrogen oxide over a platinum catalyst is very high. However, if the time of contact between the gas and the catalyst is significantly increased the NO-yield drops sharply as a result of undesirable side reactions. The optimal contact time lies between 0.0001 and 0.0002 sec. To ensure the required time of contact between the air-ammonia mixture and the catalyst the converter has a number of gauzes stacked to form a package, and the gas mixture passes through all the gauzes consecutively. For units operating at atmospheric pressure the package usually contains 3 or 4 gauzes; when elevated pressures are used a package consisting of 15-20 gauzes is employed.

The overall rate of the oxidation process, depending on the converter design and the operating conditions, is controlled by the rate of diffusion of ammonia from the core of the gas stream to the surface of the platinum and only when the agitation is very intense, by the rate of the reaction between ammonia and the oxygen absorbed on the platinum.

The intensity of catalysis, based on the rate of diffusion of ammonia in air, can be found from the equation:

$$G = \frac{D}{RTl} \quad (3.1)$$

where  $G$  is the catalysis intensity, kg-mole/m<sup>2</sup>·sec·atm;  $D$  the diffusivity of ammonia in air, m<sup>2</sup>/sec;  $R$  the universal gas constant, m<sup>3</sup>·atm/kg-mole·deg;  $T$  the temperature of the catalyst surface, °K;  $l$  the mean length of the path of a molecule in the pores of the catalyst, m.

Platinum catalysts are very sensitive to the presence of impurities, which may be introduced into the converter with the ammonia-air mixture. Phosphine, which poisons the platinum catalyst irreversibly even when its content in the gas mixture is as low as 0.00001 %, is especially toxic.

Sulphur-containing compounds poison the catalyst in part reversibly. No dust, rust, or compressor lubricant must gather on the catalyst surface. Because of this the ammonia and the air are care-

fully cleaned before being fed to the converter. However small amounts of harmful impurities still enter into the converter, and this results in a gradual drop in the catalyst activity. The catalyst is scrubbed with weak solutions of hydrochloric and nitric acids to restore the activity.

Under the conditions of the ammonia-oxidation process the platinum catalyst gradually becomes friable, its mechanical strength drops, and tiny particles of the catalyst are carried away by the

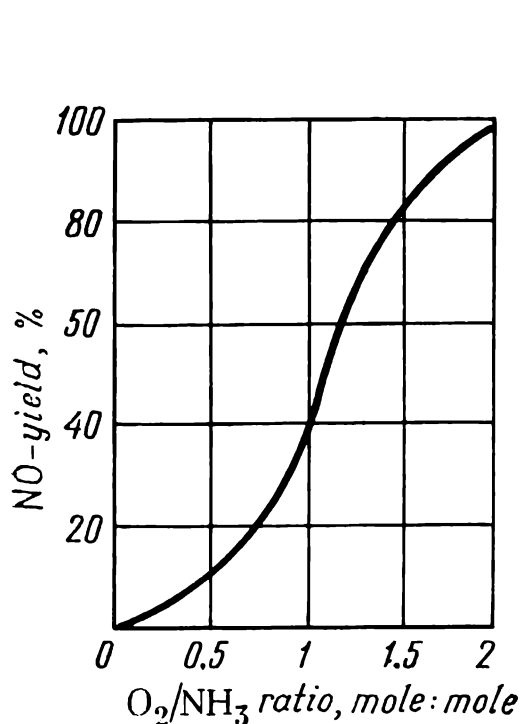


Fig. 20. Nitric oxide yield as a function of oxygen-to-ammonia ratio

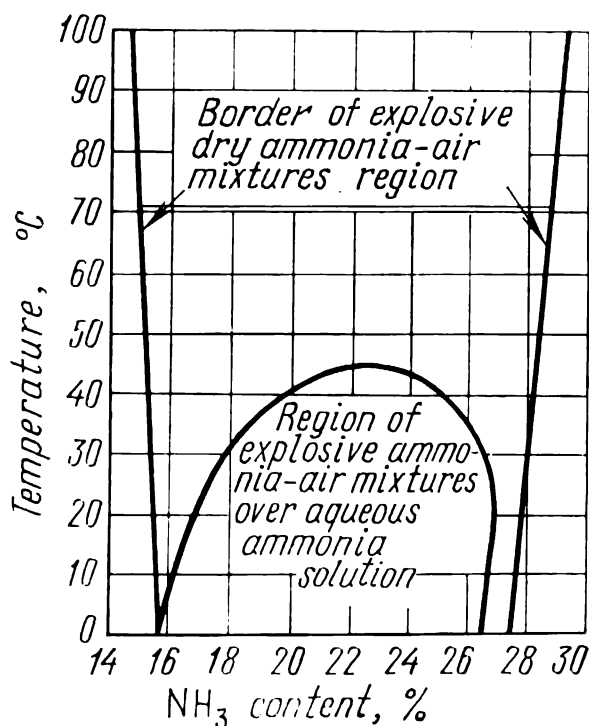


Fig. 21. Ammonia content in explosive ammonia-air mixtures

gas stream. In units operating at atmospheric pressure and at a temperature of about 800 °C losses of platinum-rhodium catalyst amount to 0.04-0.06 g per ton HNO<sub>3</sub> produced. Where the pressure and temperature are higher catalyst losses are larger. Thus, for instance, in units operating at a pressure of 8 atm and a temperature of 900 °C catalyst attrition may be as high as 0.3-0.4 g per ton HNO<sub>3</sub>.

The platinum carried away with the nitrous gases is partially recovered, however a significant part of it is lost. When the loss in weight of the gauzes grows to about 30% they are removed for remelting. Platinum-rhodium gauzes of units operating at atmospheric pressure serve about 1.5 years. The significant loss of platinum catalyst poses the urgent problem of developing and employing active non-platinum catalysts and also new schemas for their application.

According to the stoichiometry of the equation of ammonia oxidation, the air-ammonia mixture should contain 1.25 moles O<sub>2</sub> per mole NH<sub>3</sub>. To increase the nitric oxide yield and the rate of ammo-

nia oxidation a ratio of  $O_2 : NH_3 = 1.7$  to  $2.0$  is used in practice. This corresponds to an ammonia content of the air-ammonia mixture of approximately 10-12%. It should be remembered that oxygen is needed not only for oxidizing the ammonia, but also for the subsequent oxidation of nitric oxide to the peroxide. Fig. 20 shows how the nitric oxide yield depends on the ratio of oxygen to ammonia in the initial ammonia-air mixture for a platinum catalyst operating at atmospheric pressure.

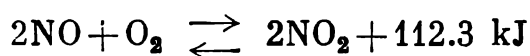
Ammonia-air mixtures are explosive within a definite interval of ammonia-to-air ratios. Fig. 21 gives the limits of  $NH_3$ -content of explosive ammonia-air mixtures at atmospheric pressure. The range of explosive mixtures of dry ammonia and air widens with an increase in temperature. The presence of water vapours in the mixture narrows the dangerous region. In industry mixtures are used which lie outside the boundaries of explosion-hazardous ammonia-to-air ratios.

Up to a certain point an increase in the temperature exerts a favourable influence on the process.

Fig. 22 shows the change in the nitric oxide yield with temperature over a platinum catalyst. For a platinum-rhodium catalyst in a unit operating at atmospheric pressure the gas temperature should be maintained between 700 and 800 °C, and at elevated pressures, from 800 to 900 °C.

Oxidation of the nitric oxide and absorption of the nitrogen peroxide with water are carried out practically simultaneously in one and the same apparatus. However, it is better to consider the relationships governing each of these processes separately.

**Oxidation of nitric oxide to the peroxide** is the second stage in manufacturing nitric acid



Below 150 °C the reaction is practically completely shifted toward formation of nitrogen peroxide. At higher temperatures the equilibrium shifts to the left, and above 800 °C there is practically no oxidation of nitric oxide to nitrogen peroxide.

Oxidation of nitric oxide to nitrogen peroxide results in a decrease in volume and the liberation of considerable amounts of heat. Consequently, lowering the temperature and raising the pressure will effect the equilibrium yield of nitrogen peroxide favourably.

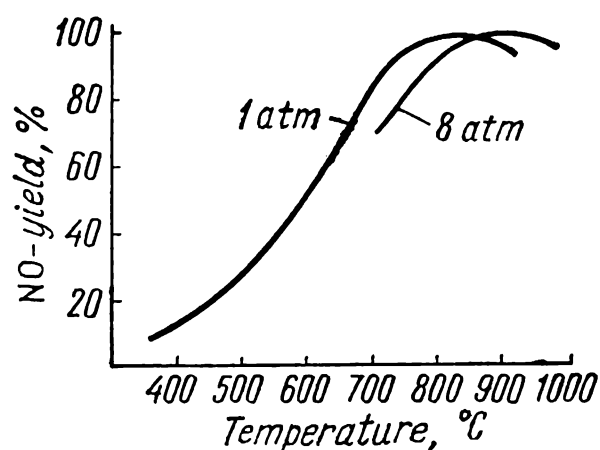
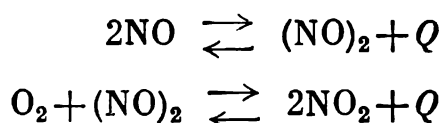


Fig. 22. Change in nitric oxide yield with temperature at  $P = 1$  atm and  $P = 8$  atm

For the great majority of reactions, raising the temperature leads to an increase in the reaction rate, but oxidation of NO to NO<sub>2</sub> does not follow the general rule—the reaction rate drops with an increase in the temperature. Several hypotheses have been postulated to explain this phenomenon; one of them—that most [widely accepted—is that oxidation of NO to NO<sub>2</sub> proceeds through the intermediate formation of the nitric oxide dimer:



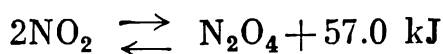
Formation of the nitric oxide dimer is a reversible reaction in which heat is liberated. Consequently, increasing the temperature shifts the reaction equilibrium to the left, the equilibrium constant is lowered, and the equilibrium concentration of the dimer in the gas mixture drops. The rate of subsequent oxidation of the dimer to nitrogen peroxide,

$$\frac{dG_{\text{NO}_2}}{d\tau} = k_1 p_{(\text{NO})_2} p_{\text{O}_2} \quad (3.2)$$

depends on  $p_{(\text{NO})_2}$ , the concentration of the dimer. It follows that the decrease in the rate of oxidation of nitric oxide to the peroxide when the temperature is raised can be explained as a result of a sharp drop in the dimer concentration.

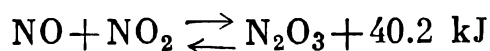
In units which operate at atmospheric pressure, nitric oxide conversion to the peroxide is about 92%, and the NO (together with NO<sub>2</sub>) is absorbed with an alkali, since complete oxidation would require a long time and correspondingly large apparatus volume.

Nitrogen peroxide can associate to form the dimer:



The rate of this reaction is extremely high and the NO<sub>2</sub> : N<sub>2</sub>O<sub>4</sub> ratio is practically determined by the reaction equilibrium. At 0 °C the equilibrium degree of association of NO<sub>2</sub> is 71%.

Nitrogen peroxide reacts with nitric oxide to form nitrogen trioxide (nitrous anhydride):

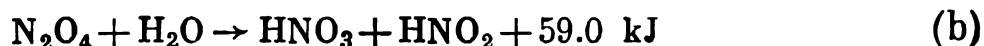
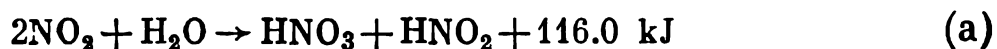


In this reaction, as in the reaction discussed above, equilibrium is established practically instantaneously. In the conditions of the industrial process the nitrous gases produced by ammonia oxidation contain only insignificant amounts of N<sub>2</sub>O<sub>3</sub>.

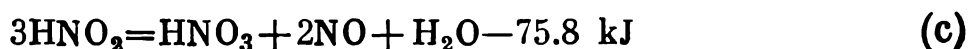
The reactions of oxidation and oxide-association form a mixture of nitrous gases which contains, besides nitrogen and oxygen introduced with the air, NO<sub>2</sub>, N<sub>2</sub>O<sub>4</sub>, N<sub>2</sub>O<sub>3</sub>, NO, N<sub>2</sub>O, and H<sub>2</sub>O. The content of the various nitrogen oxides varies sharply depending on the

conditions, but the basic component of the process of absorption with water at atmospheric pressure is  $\text{NO}_2$ .

**Absorption of nitrogen peroxide with water** is the final stage in nitric-acid production. Nitrogen peroxide and its dimer react with water as follows:



Nitrous acid is unstable and decomposes in the following manner:



The overall absorption equation is:



Nitrogen trioxide reacts with water to form nitrous acid, which decomposes by reaction (c). Nitric oxide and nitrous oxide are practically insoluble in water.

Absorption of the peroxide is a chemisorption process of mass transfer in a gas-liquid system, and all the methods for intensifying such processes discussed in Part I, Chapters 2 and 5 are applicable. Depending on the conditions the overall rate of the process may be limited by the rate of the chemical reactions or by the rate of diffusion of nitrogen peroxide in the gas phase. The diffusion stage is usually the controlling one at the end of the absorption process, when there are only small amounts of  $\text{NO}_2$  present in the gas phase.

In the course of  $\text{NO}_2$ -absorption the concentration of the nitric acid grows and with it, the vapour pressure of the nitrogen oxides over the nitric acid solution, i.e. the driving force for the process drops [see Part I, equation (2.68)]. When equilibrium is reached the process ends. Lowering the temperature and elevating the pressure have a favourable effect on absorption of nitrogen peroxide with water.

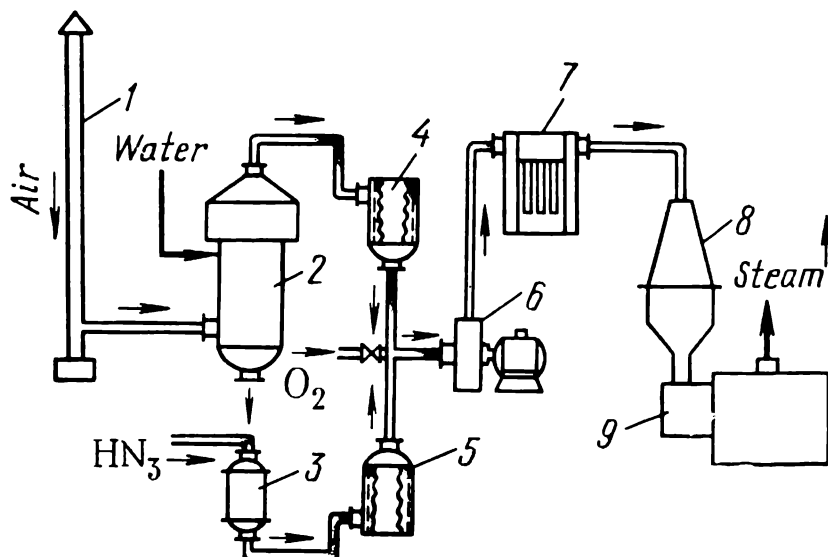
When the nitrous gases are produced in units which operate at atmospheric pressures and use ammonia-air mixtures (10-12%  $\text{NH}_3$ ), and when the  $\text{NO}_2$  is absorbed at ordinary temperatures, only dilute nitric acid, with a concentration of 47-50%  $\text{HNO}_3$ , can be obtained. By lowering the absorption temperature the equilibrium can be shifted towards formation of nitric acid with a higher concentration, but the effect is small, due to the reduced rate of reaction of the nitrogen peroxide with the water. By raising the pressure to 10 atm nitric acid containing 60-62%  $\text{HNO}_3$  can be produced.

In conversion of an air-ammonia mixture to nitric acid at atmospheric pressure the slowest stage is oxidation of the nitric oxide to the peroxide. Because of this large-size oxidation-absorption towers must be used.



Fig. 23. Flow diagram of unit for making nitric acid at atmospheric pressure:

1—air-intake pipe; 2—sieve-tray air scrubber; 3—filter; 4 and 5—cloth-cardboard filters; 6—ammonia-air blower; 7—porous-tube filter; 8—catalytic converter; 9—waste-heat boiler; 10 and 11—coolers; 12—hydroseal; 13—gas blower; 14—packed tower for acid absorption; 15—acid coolers; 16—pumps; 17—oxidation tower; 18—packed tower for alkaline absorption; 19—exhaust stack



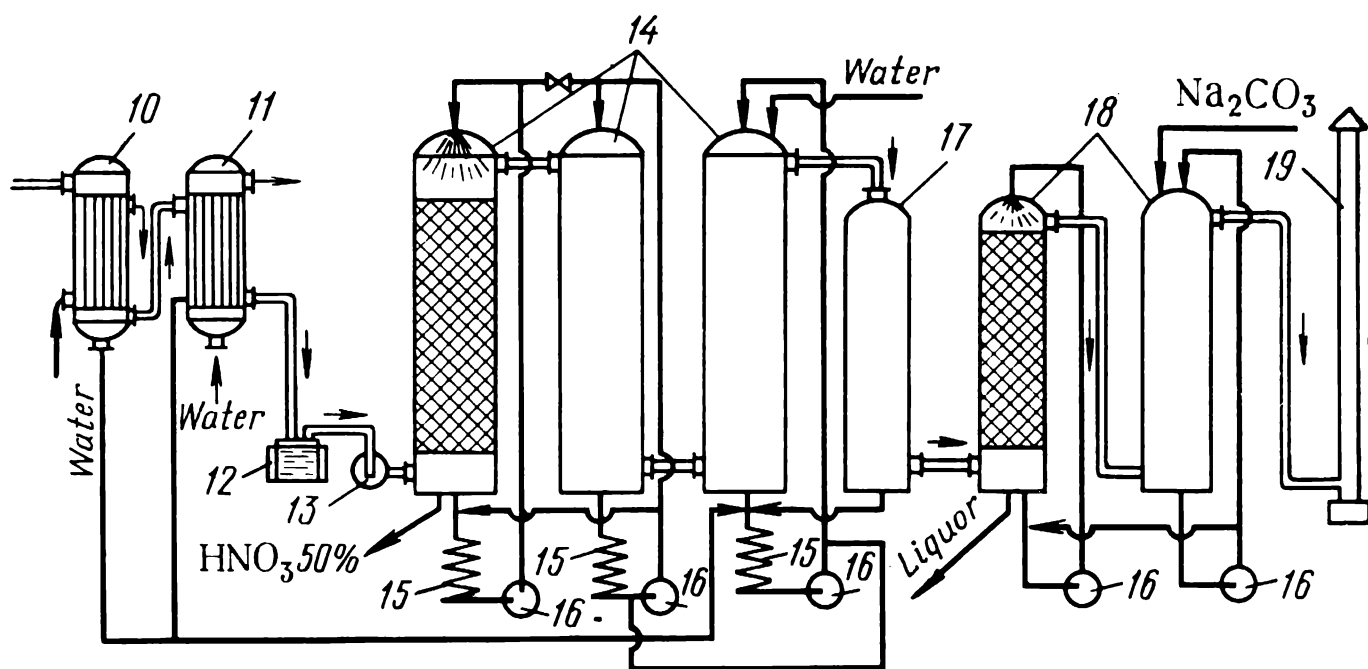
If air enriched with oxygen or pure oxygen is used in making nitric acid, nitrous gases with a higher nitric oxide content are produced and the rate of oxidation of NO to NO<sub>2</sub> is increased.

### 3. The Manufacture of Weak Nitric Acid

Plants for manufacturing weak nitric acid from ammonia can be divided into (1) units operating at atmospheric pressure; (2) units operating at elevated pressures, and (3) pressure-combination units, in which ammonia is converted at atmospheric pressure and oxidation of NO and absorption of NO<sub>2</sub> with water are carried out under an elevated pressure. The flow diagram of a unit for manufacturing weak nitric acid at atmospheric pressure is given in Fig. 23.

The air enters through an intake pipe, which is usually located outside the plant territory. A sieve-tray froth scrubber and cardboard filter remove particles and chemical impurities from the air.

Particles and oil are removed from the ammonia in a coke filter and a cardboard filter. Air, ammonia and supplementary oxygen are forced through the system by an ammonia-air blower in amounts which give a gas mixture containing 10-12% NH<sub>3</sub>. The mixture then passes through a filter, where it is purified by filtering through porous ceramic tubes, and enters the catalytic converter at the top. The platinum-rhodium wire gauze is located in the central part of the converter (see Part I, Fig. 98). Conversion of ammonia to nitric oxide is close to 97-98%. The temperature of the nitrous gases leaving the converter is usually maintained at approximately 800 °C. In the waste-heat boiler the gas temperature drops to 250 °C. The gases are then cooled further with water in tube-and-shell coolers to approximately 30 °C. This is accompanied by partial condensation of water vapour present and by oxidation of nitric oxide. The degree of NO-

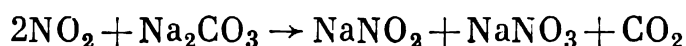
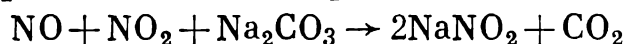


oxidation in the first cooler is very small and the acid produced contains only 3%  $\text{HNO}_3$ . The acid from the second cooler has a concentration of 25%  $\text{HNO}_3$ .

After passing through a hydraulic seal the nitrous gases are fed to the absorption section of the unit by a gas blower. Here they pass through consecutive acid-absorption towers, with a packing of acid-resistant rings. The towers are furnished with coolers, for lowering the temperature of the acid leaving the towers, and with pumps, for circulating the acid. The number of acid-absorption towers is usually from six to eight.

Water for absorbing  $\text{NO}_2$  is fed to the last of the towers (in the direction of the gas flow); the acid consecutively passes through all the towers countercurrent to the gas stream and leaves the first tower with a concentration of 50%  $\text{HNO}_3$ . Approximately 92% of the nitrogen oxides entering the absorption system is absorbed in the acid towers. Following the acid towers there is an oxidation tower for oxidizing  $\text{NO}$  to  $\text{NO}_2$ . After passing through this tower the nitrous gases go on to alkali-absorption with an aqueous soda solution.

In the alkali-absorption towers both nitrogen peroxide and a  $\text{NO}_2$ -plus- $\text{NO}$  mixture ( $\text{N}_2\text{O}_3$ ) are absorbed; there is no desorption of  $\text{NO}$  to the gas phase as in absorption with water



A sodium-nitrate plus nitrite solution is brought out from the first alkali-absorption tower (in the direction of gas flow) for further processing. At some plants milk of lime is used in place of a soda solution for alkali absorption and calcium nitrate and nitrite are formed. All the packed towers operate with very little axial mixing of the gas and liquid streams. This means that an ideal plug flow

model can be used for them both. A simplified flow diagram of a plant for manufacturing weak nitric acid at elevated pressures (7.3 atm) is given in Fig. 24.

Air from the atmosphere passes through an apparatus for cleaning it and enters an axial-type compressor with a gas-turbine drive. The air is compressed to 7.3 atm with a temperature rise to 135 °C and flows through an air heater where the temperature is raised further

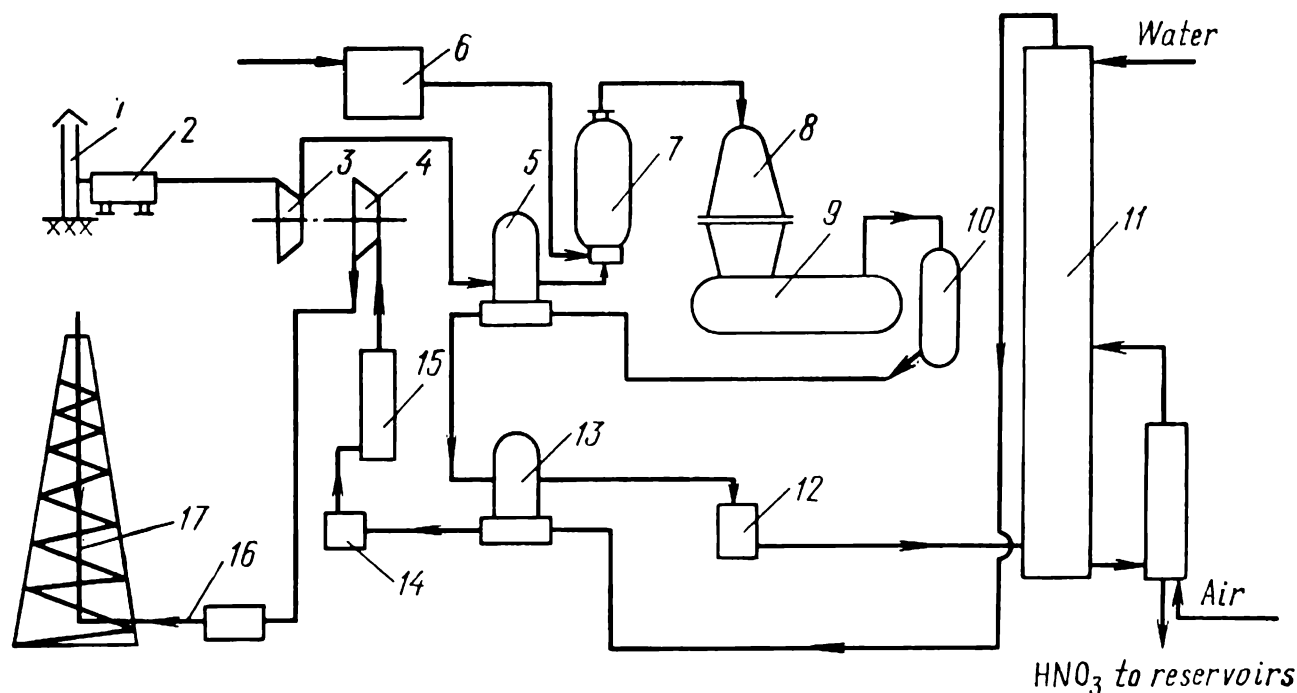


Fig. 24. Simplified flow diagram of a plant for manufacturing weak nitric acid under a pressure of 7.4 atm:

1—air-intake pipe; 2—air-purification apparatus; 3—gas compressors; 4—gas turbine; 5—air heater; 6—ammonia pretreatment apparatus; 7—mixer with a filter; 8—converter; 9—waste-heat boiler; 10—oxidizing unit with a filter; 11—absorption tower; 12—cooler-condenser; 13—stack gas heater; 14—combustion chamber; 15—catalytic-purification reactor; 16—waste-heat boiler; 17—stack

to 250 °C at the expense of the excess heat of the gases leaving the nitrous gases oxidizing unit. In the mixer the air is added to the ammonia flowing from the combination unit, which serves as an evaporator, filter and heater. From the mixer the ammonia-air mixture flows to the converter, where at a temperature of 890-900 °C the ammonia is oxidized on a platinum gauze. The nitrous gases, which contain 9.0-9.6% NO, go on to the waste-heat boiler.

They then flow through an oxidizing unit in whose upper part there is a filter (of glass wool) for recovering entrained platinum, the air heater, where they are cooled to 210-230 °C, the stack gas heater, which lowers their temperature to 150-160 °C and the cooler-condenser, where the temperature of the nitrous gas drops to 45-50 °C. The cooled nitrous gas enters into the absorption tower—an apparatus 2 m in diameter, 46 m high with 49 sieve trays—at the bottom. There are coils on the trays through which water is recycled to remove heat.

Cooled condensate is fed to the top tray and flows down through the tower in countercurrent with the gas, absorbing nitrogen oxides and forming nitric acid on its way. The acid formed flows by force of gravity to a stripping tower, where by blowing hot air through the acid dissolved nitrogen oxides are desorbed and returned to the absorption tower entering it at the 6th tray from the bottom. The gas effluent from the absorption tower passes through the stack gas heater and is then subjected to catalytic purification.

The content of nitrogen oxides in the gas leaving the absorption tower is from 0.05 to 0.1% (vol). The effluent gas at 110-120 °C enters a combustion chamber, where it is heated to 380-480 °C by mixing it with the hot products of burning natural gas in air. The gas mixture then goes to a purification reactor, where hydrogen compounds in the gas undergo combustion and the nitrogen oxides are reduced to elemental nitrogen in two beds of catalysts (palladiumized aluminium oxide and activated alumina). The temperature of the effluent rises to 700-710 °C. The purified gas passes through a filter to remove entrained catalyst and flows to a turbine, where its pressure is reduced to approximately the atmospheric level, and heat energy is converted to mechanical energy, utilized to rotate the impeller of the air compressor. The effluent gas then passes through a waste-heat boiler and is discharged to the stack.

Units operating at elevated pressure have a number of advantages, as compared to units which operate at atmospheric pressure:

1. The conversion of the nitrogen oxides to nitric acid is raised to 98-99% and the concentration of the nitric acid produced—to 60-62%. Alkali absorption is unnecessary.
2. The volume of the absorption towers is tens of times less than that of packed towers operating at atmospheric pressure.
3. Capital investments and amounts of high-alloy steels used in the apparatus are lower.
4. Operation of the unit is simpler.

However, the increased catalyst and power consumptions at elevated pressures are serious disadvantages of high-pressure systems, which have limited their wider use. Due to this factor, in the last few years flow schemes in which catalytic conversion of the ammonia is carried out at a lower pressure (of up to 4 atm) than is used for oxidizing the nitrogen oxide (up to 12 atm) have been most often used. Characteristic features of a modern unit are large production capacity with one line of equipment (380-400 thousand tons per year) and maximal employment of the energy of effluent gases and low-potential heat for technological needs so as to obtain an autothermal technological process. The flow diagram of a combination system operating at pressures of 4 and 10 atm is given in Fig. 25. Air compressed and heated (4.2 atm and 200 °C) in a centrifugal compressor is passed through the jacket of a catalytic converter combined



the absorption tower each tray of which is cooled using recycled cooled water. The 60%-concentration nitric acid produced is passed through a stripper tower and then to a storage reservoir. The gases from the stripper are returned to the cycle; they are mixed with the nitrous gas upstream of the scrubber.

The gas effluent from the absorption tower passes through a heater, where its temperature is raised by means of a mixture of the purified gas and combustion products, then on through a mixer, where natural gas is added, and through a catalytic clean-up apparatus containing a palladium catalyst. The content of nitrogen oxides at the exit from this clean-up unit is brought down to 0.004-0.006%. The purified gas at a temperature of 750-770 °C is fed to a recuperation turbine which drives the air and nitrogen-oxides-gas compressors. The purified gas flows to a fire box, where natural gas is burned in the amount necessary to cover the deficiency of heat, then through the heater of the absorber effluent gas it is discharged to the ambient air through a 100 m high stack.

#### 4. The Manufacture of Concentrated Nitric Acid

Concentrated  $\text{HNO}_3$  with an  $\text{HNO}_3$ -content above 96% is used in a number of manufacturing processes. Nitric acid of such concentration can be obtained either by concentrating dilute nitric acid or by direct synthesis.

##### Concentrating nitric acid.

Fig. 26 shows the boiling points of aqueous nitric-acid solutions at atmospheric pressure. As is evident from the diagram, a maximum boiling point of 121.9 °C is reached at an  $\text{HNO}_3$ -content of 68.4%. At this point the composition of the vapour coincides with that of the liquid phase and it is not possible to further increase the nitric-acid concentration by fractional distillation. Usually concentrated nitric acid (over

68%  $\text{HNO}_3$ ) is made by distilling dilute nitric acid in the presence of high-strength sulphuric acid, used as a dehydrating agent. The high-strength sulphuric acid combines with the water contained in the dilute nitric acid to form hydrates of sulphuric acid, which boil at a temperature higher than the boiling point of 100%  $\text{HNO}_3$ . Consequently, conditions can be selected for heating such a mixture under which the gas phase will consist almost entirely of nitric acid.

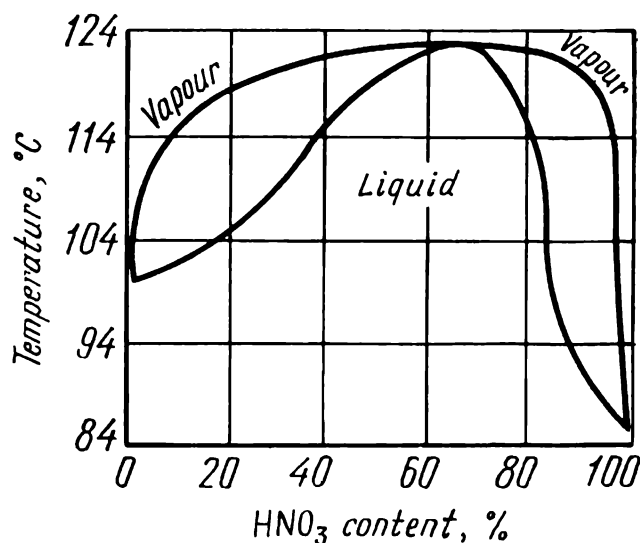


Fig. 26. Boiling-point diagram for aqueous nitric-acid solutions at atmospheric pressure

Fig. 27 is a phase diagram of the  $\text{H}_2\text{O}$ - $\text{HNO}_3$ - $\text{H}_2\text{SO}_4$  three-component mixture, with curves for constant vapour-phase content plotted on it. It follows from the diagram that as the content of  $\text{H}_2\text{SO}_4$  in a three-component mixture with a fixed content of nitric acid in the liquid rises, the fraction of  $\text{HNO}_3$  in the vapour increases and that of  $\text{H}_2\text{O}$  decreases.

Distillation of dilute nitric acid together with concentrated sulphuric acid (92-94%  $\text{H}_2\text{SO}_4$ ) is carried out both in tray-type bubbling

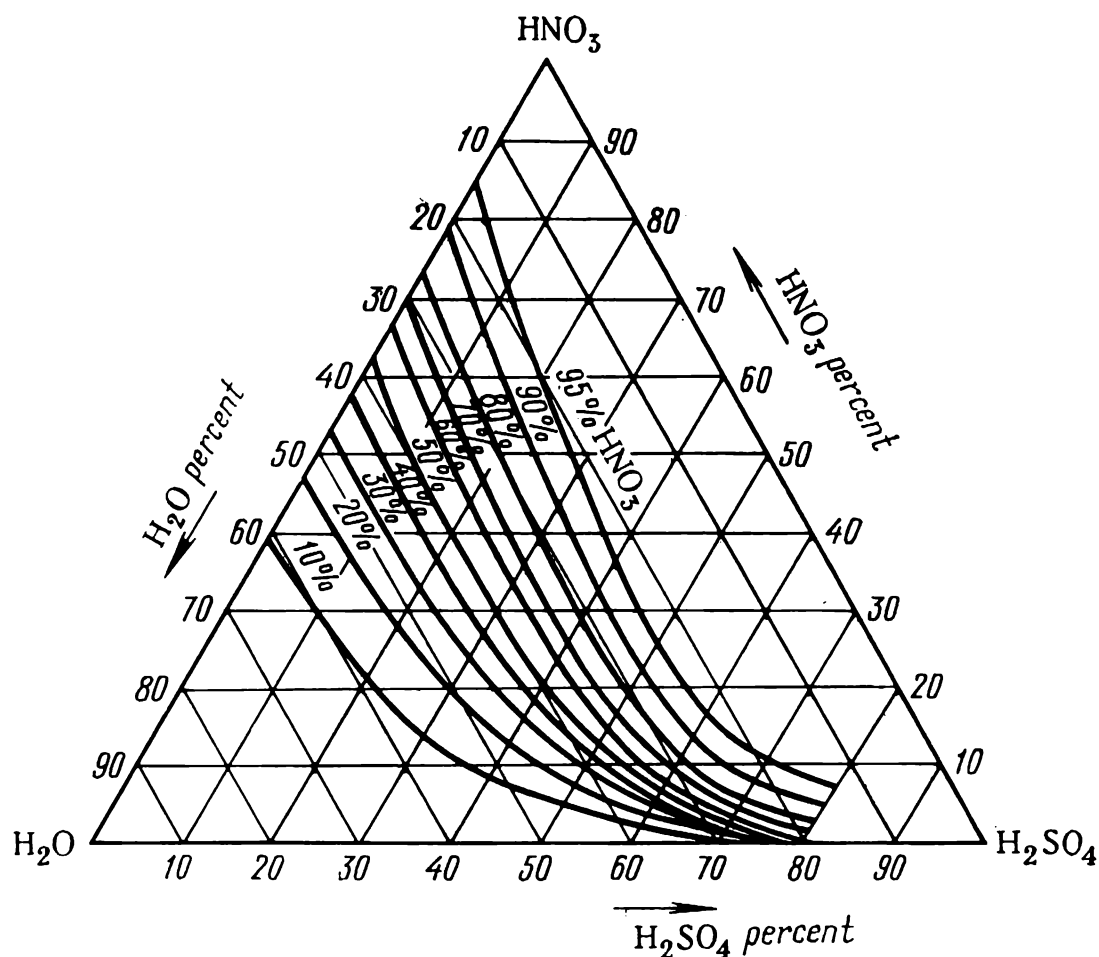


Fig. 27. Composition of the vapours over three-component ( $\text{H}_2\text{O}$ - $\text{HNO}_3$ - $\text{H}_2\text{SO}_4$ ) mixtures

columns and in columns with a ring packing. The columns are made of acid-resistant ferrosilicon cast-iron containing 14-18% Si; this material is not corroded by mixtures of sulphuric and nitric acids at high temperatures.

Fig. 28 is a flow diagram of a unit for concentrating weak nitric acid. The sulphuric acid is fed to one of the top trays of a tower. Somewhat lower dilute nitric acid, containing approximately 50%  $\text{HNO}_3$ , is fed to the tower. Part of it passes through an evaporator. The mixture is heated with direct steam (180-200 °C) introduced at the bottom of the tower. Nitric-acid vapours containing small amounts of water vapour and nitrogen oxides, formed by decomposition of the nitric acid, flow from the tower to a condenser, where the nitric acid

condenses, whereas the nitrous gases (nitrogen oxides) pass on to an absorber. Some of the nitrogen oxides dissolve in the nitric acid, and because of this the acid from the condenser is returned to the upper trays of the tower, where these gases are stripped from it, after which it is withdrawn, as the product, to a cooler.

The spent dilute sulphuric acid (70% concentration) flows out of the bottom of the tower and goes directly to an evaporator without

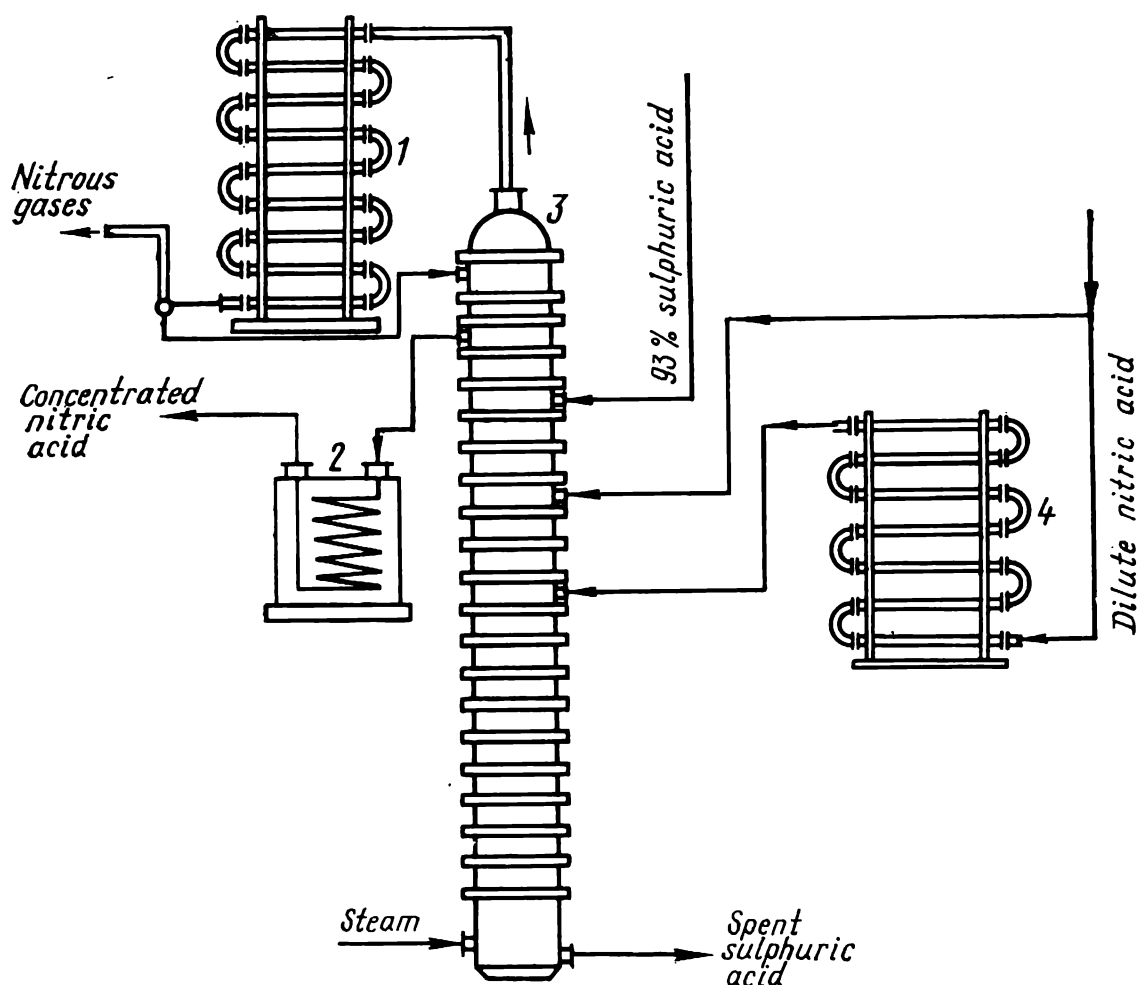
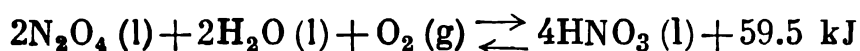


Fig. 28. Flow diagram of unit for concentrating dilute nitric acid:  
1—condenser; 2—cooler; 3—tray-type concentrating tower; 4—dilute nitric acid evaporator

cooling. Consumption of concentrated sulphuric acid is 3-4 tons per ton nitric acid. To return the sulphuric acid to the process its concentration must be raised to the vitriol oil level. Consumption of large amounts of fuel, losses of sulphuric acid and corrosion of the apparatus are accompanying factors. Because of this much attention is being devoted to manufacturing concentrated nitric acid by direct synthesis processes.

**Direct synthesis of concentrated nitric acid** proceeds by the reaction:



This process is carried out in special-type autoclaves at a temperature of about 75 °C and a pressure of 50 atm.

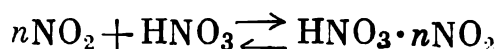


To shift the reaction equilibrium towards formation of nitric acid and to increase the reaction rate there must be an excess of liquid nitrogen peroxide (tetroxide) in the mixture entering the autoclave. Usually a 25 per cent excess of liquid nitrogen peroxide with respect to the stoichiometric amount is used. The excess nitrogen peroxide, which does not participate in the reaction, is separated from the 98-99% nitric acid formed and returned to the manufacturing process.

The most complex stage in making concentrated nitric acid by direct synthesis is that in which liquid nitrogen peroxide is obtained. This is accomplished by condensing nitrous gases under cooling and pressure or by their absorption in concentrated nitric acid at low temperatures followed by desorption of the nitrogen peroxide from the nitric acid, and then cooling to convert it to the liquid state.

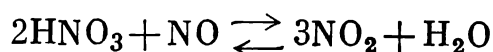
For producing liquid nitrogen peroxide by direct condensation the nitrous gases must have a high initial content of the nitrogen oxides and the NO must be completely oxidized to NO<sub>2</sub>. In industrial conditions the gas is cooled to a temperature not lower than -8 °C because of the danger of formation of N<sub>2</sub>O<sub>4</sub> crystals which can plug the apparatus.

The second method for separating nitrogen peroxide from the nitrous gases and obtaining it as a liquid is based on the high solubility of nitrogen peroxide in concentrated nitric acid (97-98% HNO<sub>3</sub>):



The product of the reaction is known as nitro-oleum.

Nitric oxide reacts with concentrated nitric acid by the reaction



At a 10-11% content of nitrogen oxides in the nitrous gases by absorbing them with 98% nitric acid a solution can be obtained which contains up to 30% NO<sub>2</sub>. If this solution is heated to 80 °C, the nitrogen peroxide separates from it in gaseous form and can then be condensed by cooling. In industrial conditions condensation is usually carried out in two consecutive coolers: first in a water cooler and then in one cooled with brine [Ca(NO<sub>3</sub>)<sub>2</sub> + H<sub>2</sub>O] to -8 °C. It is necessary to lower the temperature to -8 °C because of the presence of a small amount of inert gases in the nitrogen peroxide.

It follows that the manufacture of concentrated nitric acid by direct synthesis (the nitro-oleum process) consists of the following basic steps:

- (1) producing nitrous gases by catalytic oxidation of ammonia;
- (2) separating the excess water from the nitrous gases;
- (3) oxidizing NO of the nitrous gases to NO<sub>2</sub>;
- (4) finally oxidizing the NO-remainder with concentrated nitric acid;

(5) cooling the nitrous gases and concentrated nitric acid to approximately  $-10^{\circ}\text{C}$  prior to absorption;

(6) absorbing the nitrogen peroxide in concentrated nitric acid (production of nitro-oleum);

(7) desorbing the nitrogen peroxide from the nitro-oleum by heating;

(8) condensing the nitrogen peroxide by cooling (obtaining liquid nitrogen tetroxide,  $\text{N}_2\text{O}_4$ );

(9) processing the liquid nitrogen tetroxide with water and oxygen in an autoclave under a pressure of 50 atm and at a temperature of  $75^{\circ}\text{C}$ ;

(10) stripping the nitrogen peroxide, taken in excess for the reaction and dissolved in the concentrated nitric acid (98-99%  $\text{HNO}_3$ ) formed in the autoclave, by heating. This is known as bleaching of the concentrated nitric-acid end product.

### 1. The Types of Inorganic Salts and Their Uses

Hundreds of different inorganic salts are used in agriculture, in industry and in the home, and the number is continuously growing. The mining and manufacture of salts are carried out on a very large scale; some of the inorganic salts and fertilizers are multitonnage chemical products, with production figures of millions and even tens of millions of tons per year. Chemical compounds of sodium, phosphorus, potassium, nitrogen, aluminium, iron, copper, sulphur, chlorine, fluorine, chromium, and barium are produced and consumed in the largest volumes.

Inorganic salts are classified according to their origin (naturally occurring or synthetic), composition (salts of sodium, phosphorus, etc.), methods of production, and also their uses. The main field of consumption of inorganic salts is agriculture, and inorganic fertilizers and pesticides are manufactured in the largest amounts. Industry uses very many different salts, some on a very large scale. The chemical industry not only manufactures inorganic salts but is one of the chief consumers, especially of salts of sodium. Common salt is used in huge quantities; it is the principal raw material in producing chlorine, calcinated soda, hydrochloric acid and caustic soda. Sodium sulphate is a raw material in making sodium sulphide and glass. Sodium sulphide, various sulphites (sodium thiosulphate, sulphite and hydrosulphite), sodium fluorides, sodium and potassium bichromates, sodium phosphates, as well as many other salts—of iron, aluminium, barium—are employed in the manufacture of dyes, reagents, catalysts, synthetic fibres, plastics, rubber, detergents and other chemical products.

In metallurgy inorganic salts are used in enriching and hydrometallurgical processing of ores, as fluxes and additives in smelting processes, in obtaining metals by electrolysis, in processing the surface of metals, in soldering and welding metals and their alloys, etc.

The glass industry consumes large quantities of sodium sulphate, a basic component of the charge from which the glass is made, and also salts and oxides of boron, lead, zinc, and barium, used to give a glass specific desired properties. In the manufacture of cements, ceramics and refractories, inorganic salts are important raw materials. The mining and ore-dressing, pulp-and-paper, textile, leather,

pharmaceutical and other industries are consumers of various inorganic salts. In short, there is practically no branch of industry which is not a user of inorganic salts.

## 2. Methods Used in Manufacturing Inorganic Salts and Typical Processes of Salts Technology

Industrial salts are obtained either by mining naturally occurring salts or by producing the salts from naturally occurring, or other, raw materials.

The mining and processing of naturally occurring soluble salts (halurgy) are based on a combination of leaching, evaporation, crystallization and dehydration operations, used in treating solutions of naturally occurring salts. By such operations a system of salts is divided into the individual components.

The foundation of the science of salt systems was laid by L.G. van't Hoff, N.S. Kurnakov and their followers in works devoted to the physicochemical analysis of salt systems, i.e. the laws governing the relationships between composition, phase states and properties of such systems. Using solubility diagrams (see Part I, Chapter 5) one can determine the conditions for crystallization of salts from their solutions.

Salts are found in nature either in the form of deposits or in solutions (brines) in lakes, seas and ground waters. The principal components of salt deposits and of brines (sea water, salt lakes) are sodium chloride, sodium sulphate, chlorides and sulphates of potassium, magnesium and calcium, salts of boron and bromine, and carbonates (naturally occurring soda).

Mining and underground leaching are the principal methods used to obtain the naturally occurring solid salts. Mining is carried out either by the open-pit or shaft method, depending on the depth of the deposits. Mining is employed to obtain rock-salt, sodium sulphate (thenardite), naturally occurring magnesium and potassium salts (sylvinite, carnallite), etc. Underground leaching yields the salts in the form of brines (used chiefly in winning sodium chloride). This method is economically advantageous when the salt is to be processed in solution—in manufacturing soda ash, chlorine and caustic soda, etc. Underground leaching is carried out by dissolving the salt layers with water pumped into the deposit through drill wells.

Natural brines result from the solution of salt deposits by ground water. The natural brines are won by pumping them up through drill wells using deep-well pumps or compressed air (air lift). The concentration of the salt in a naturally occurring sodium-chloride brine used in manufacturing soda ash or chlorine is raised by dissolving rock-salt in it in a saturator reservoir, after which the brine is

purified. Occasionally naturally occurring brines are evaporated to obtain solid "evaporated" salts from them.

The brines of salt lakes and bays, which contain sodium chloride, sodium sulphate, salts of magnesium, bromine and boron and also natural soda, are a major source of a number of these salts. The salts are won in the form of "self-deposited" salts, i.e. salts which crystallize out in nature, or by the basin method, in which shallow artificial basins are used to evaporate water from the brines and deposit the salts.

Many different processes are employed to manufacture the tremendous variety of industrial salts. However the flow diagrams of the processes for making almost all of them are made up of unit operations typical for industrial salts technology. **The unit operations employed in inorganic-salts technology** are size reduction of solid materials (raw materials, sinters), beneficiation of raw materials, drying, calcining, sintering, dissolution, leaching, sedimentation, filtration, evaporation, cooling of solutions, crystallization. These processes are typical of all inorganic-salt manufacturing processes. Absorption and desorption are also often employed in the technology of inorganic salts.

Most unit operations are based on physical processing methods, especially in the stages of preparing the raw material and final treatment of the product. The formation of the mineral salts, on the other hand, results from chemical reactions which take place in the course of roasting, sintering, leaching or absorption. The leaching of naturally occurring materials (or sinters) is accompanied by exchange reactions, roasting by oxidation-reduction reactions. The synthesis of salts based on chemisorption processes involves neutralization reactions.

The majority of operations used in manufacturing salts are diffusion limited and they are governed by the general equation for mass transfer

$$u = kF \Delta C \quad (4.1)$$

To intensify the processes employed in making inorganic salts use is made of all the techniques for increasing the driving force  $\Delta C$  and developing the interface area between reactants  $F$  (see Part I, Chapters 2 and 5). A characteristic feature of salts technology is processing in liquid-solid systems (L-S). A highly developed interface between the phases of the L-S system is most often obtained by size reduction of the solid and stirring the suspended, fine particles of the solid in the liquid with mechanical or pneumatic agitators. The stirring promotes the process by simultaneously turbulizing the system and replacing molecular diffusion with convective transfer. Diverse means for raising the initial concentrations of the solid, liquid or gaseous reactants are used to increase the mass-transfer driving force.

An increase in the mass-transfer coefficient  $k$  is achieved in salts-technology processes mainly by means of stirring and raising the temperature. High temperatures in many cases are a means used for sharply speeding-up diffusivity and increasing the interface between phases by converting the reactants to another phase state (for example, by melting solid initial materials).

A characteristic feature of salts technology is the practically total absence of catalytic processes, whereas in manufacturing sulphuric acid, ammonia and nitric acid, discussed above, catalysts are the principal means for intensifying and for carrying out the basic operations of the manufacturing process.

Naturally occurring minerals, intermediate products of chemical industries and industrial waste products serve as the raw materials from which inorganic salts and fertilizers are manufactured. In manufacturing salts, naturally occurring minerals are the principal raw materials used. Phosphoric, potassium and boron fertilizers, sodium sulphide, sodium and potassium bichromate, ammonia sulphate and many other salts are obtained by processing naturally occurring phosphates, barites, borates, chromites, nepheline, and other naturally occurring salts of sodium, potassium and magnesium.

Not only such physical processes as leaching, evaporating and crystallizing are used to transform the raw material to the final product, but also chemical exchange-decomposition and oxidation-reduction reactions. One of the methods used in developing the ores, i.e. in transforming the useful components from an insoluble state to a chemically active one, consists in decomposing them with acids or alkalis, or sintering them with alkalis. This method is based on exchange reactions. The products of the reaction are separated utilizing differences in solubilities or the volatility of one of the components. Decomposition of naturally occurring phosphates with acids, in which insoluble salts of phosphorus are transformed into water-soluble compounds, can be cited as an example.

Many methods used for developing naturally occurring raw materials are based on redox reactions; roasting processes—oxidation, reduction, and chlorination roasting—belong to this category. The manufacture of sodium and barium sulphites by reduction roasting of sodium and barium sulphates and the manufacture of chromates by oxidation roasting of chromite ores are typical examples.

Air is employed in manufacturing salts—it is an inexhaustible source of oxygen for oxidation roasting of ores and a source of nitrogen in making nitrogenous fertilizers.

*In manufacturing salts by chemical synthesis* intermediate products of the basic chemical industries or waste products of various processes usually serve as the raw materials. Salts are synthesized

mainly using neutralization reactions. Such reactions are employed, for instance, to produce highly important nitrogenous fertilizers from acids and bases.

A large number of salts are obtained as by-products of various manufacturing processes. For instance potash ( $K_2CO_3$ ) and soda ( $Na_2CO_3$ ) are obtained as by-products in making alumina from nepheline. Diverse sulphites are produced using the  $SO_2$  contained in waste gases of non-ferrous metallurgy and sulphuric-acid plants. Calcium nitrate, which is employed as a fertilizer, can be produced from waste nitrous gases of sulphuric-acid and nitric-acid plants. Many examples can be given of such integral utilization of raw materials, in which salts are obtained together with other chemical products.

### 3. Classes of Inorganic Fertilizers

Inorganic fertilizers are salts which contain elements essential for plant growth and which are introduced into the soil to obtain large crops regularly. About 60 of the elements are found in the composition of the various plants. Primarily, carbon, oxygen and hydrogen, which make up the principal part of plant matter, and also nitrogen, phosphorus, potassium, magnesium, sulphur, calcium and iron are utilized in formation of plant tissue, and are necessary for normal growth and development of plants. The air and the soil are the sources of the plant nutrients. It is from the air that the plant, by photosynthesis, takes up the principal part of its carbon (in the form of carbon dioxide), whereas from the soil it derives water and various minerals. Part of the carbon dioxide is also obtained from the soil, through the plant roots.

Nitrogen-, phosphorus- and potassium-containing minerals are especially important for normal plant life. These elements stimulate processes of metabolism in the plant cells, growth of the plant and especially its fruits, increase the content of such valuable plant components as the starch of potatoes, sugars of beets, fruits and berries, protein of grains, and increase resistance to frost, drought and diseases.

Intensive farming results in exhaustion of the soil, i.e. the content of the mineral substances which are assimilated by plants is depleted; primarily this refers to compounds of nitrogen, phosphorus and potassium, which are soluble in water and in acids contained in the soil. Soil exhaustion leads to low crops and low quality of farm products. The decrease in the nutrient content of agricultural soils must be continually compensated for by introducing fertilizers.

Due to the tremendous scale of their use, inorganic fertilizers are the products manufactured by the chemical industry in the

largest amounts, their annual rate of production is measured in tens of millions of tons.

**Inorganic fertilizers are classified** according to the role they play in soil chemistry, the number and types of nutrient elements they contain, their physicochemical properties and, in particular, their solubility in soil water, their physiological effect on the soil to which the fertilizer is applied, method used for manufacturing them, etc.

They are classified as direct or indirect fertilizers according to their agrochemical nature. Direct fertilizers contain the nutrient elements in the form of compounds which are directly assimilated by plants. Indirect fertilizers are substances which are introduced into the soil mainly to improve its mechanical, chemical or biological properties. Ground dolomite and limestone, used to reduce soil acidity, and gypsum, used to improve the properties of soils with a high salt content, are examples of indirect fertilizers.

Direct fertilizers are classified, according to the nutrient element they contain, as phosphatic, nitrogenous, potash, magnesium, etc. According to the number of basic nutrient elements (phosphorus, nitrogen and potassium) in them, they are classified as simple fertilizers, i.e. containing only one nutrient element, or double or triple fertilizers, containing respectively two or three elements. The latter are also known as complete fertilizers since they contain all the principal nutrient elements.

Microfertilizers which contain the elements boron, manganese, zinc, and copper, needed in very small amounts to stimulate the plant growth, comprise a special, separate class. These fertilizers are introduced into the soil in amounts of less than 1 kg/hectare.

Fertilizers containing several nutrient elements and obtained by mechanical mixing of various fertilizers are known as mixed ones. Fertilizers containing several nutrient elements which are produced by chemical reactions are known as complex fertilizers.

According to their solubility in the moisture in the soil, fertilizers can be classed as water-soluble or soluble in soil acids. All nitrogenous and potash fertilizers are soluble in water. These fertilizers are readily assimilated by plants, but they are quickly washed out of the soil by surface water. Most phosphates belong to the class of fertilizers soluble in soil acids. They are dissolved much slower, but are retained in the soil much longer.

According to their physiological effect on the soil to which they are introduced, fertilizers are classified as physiologically acid, physiologically alkaline or physiologically neutral. The latter do not change the pH of the soil. According to their form (or physical properties) fertilizers are subdivided into powder-form and granulated ones. Granulated fertilizers are less hygroscopic, they do not cake during storage, are not subjected to weathering after



being introduced into the soil and are retained by the soil for a longer time—are not washed out quickly by rains. Moreover, they can be added to the soil using fertilizer machines or seed drills.

The fertilizers manufactured on the largest scale using typical methods of inorganic-salts technology are superphosphate and the principal nitrogen fertilizers—ammonium nitrate and urea.

#### 4. Phosphatic Fertilizers

The various phosphatic fertilizers, depending on their composition, have different solubilities in soil solutions and are therefore assimilated by plants differently. According to their solubility they are classed as water-soluble, available or insoluble. Simple and double (triple) superphosphates belong to the water-soluble group. Precipitate, calcined phosphate, fused phosphates and basic slag belong to the group of available fertilizers.

*Insoluble fertilizers* contain non-readily available phosphorous salts, which are soluble only in strong inorganic acids. Representatives of this group are phosphatic meal, apatites, bone meal.

*The raw materials* in manufacturing elemental phosphorus, phosphatic fertilizers and other phosphorus-containing compounds are naturally occurring phosphates—apatites and phosphate rock. The phosphorus in these minerals is in an insoluble form, mainly in the form of fluorapatite  $\text{Ca}_5\text{F}(\text{PO}_4)_3$  or hydroxylapatite  $\text{Ca}_5\text{OH}(\text{PO}_4)_3$ .

*Apatites* are usually found in concentrated deposits. The largest apatite deposits in the world are on the Kola peninsula in the USSR. In this deposit the apatite is found together with nepheline  $(\text{Na}, \text{K})_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$  and other minerals. The apatite-nepheline ore is separated by flotation into an apatite concentrate, containing 39-41%  $\text{P}_2\text{O}_5$ , and a nepheline fraction with a 30%  $\text{Al}_2\text{O}_3$  content—a raw material for making aluminium.

*Phosphate rock* is found as an ore of sedimentary origin mainly in the form of fluorapatite together with various impurities. The  $\text{P}_2\text{O}_5$ -content of concentrated phosphate rock lies between 20 and 30 per cent. Some finely ground phosphate is utilized directly as a fertilizer, known as phosphatic meal.

To obtain fertilizers which contain the phosphorus in a readily available form and which can be applied to any soil the insoluble phosphoric salts of the naturally occurring phosphate must be transformed into water-soluble or available salts. This is the basic problem which is solved in the technology of phosphatic fertilizers.

The solubility of phosphoric salts increases with increasing acidity of the salt. The neutral salt  $\text{Ca}_3(\text{PO}_4)_2$  is only soluble in mineral acids;  $\text{CaHPO}_4$  is soluble in organic soil acids and the most acid salt,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ , is soluble in water. Naturally, therefore, in manu-

facturing phosphatic fertilizers it is desirable to convert as large a part of the phosphorus as possible into monocalcium phosphate,  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ .

The transformation of the insoluble naturally occurring phosphates into soluble forms is accomplished by decomposing them with acids or bases or by heating (sublimation of the phosphorus). The technology must be aimed not only at obtaining a soluble salt but also at producing a phosphatic fertilizer with the highest possible concentration of phosphorus in it.

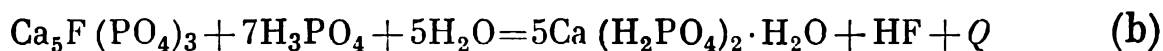
**The manufacture of superphosphate.** The chemical industry makes two kinds of superphosphate—simple and triple superphosphates. The simple superphosphate is one of the most widely used inorganic fertilizers. It is a powder (or in the form of granules) gray in colour, which contain mainly monocalcium phosphate  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  and calcium sulphate  $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ . Superphosphate also contains a number of impurities—phosphates of iron and aluminium, silica and also phosphoric acid. The manufacture of superphosphate consists essentially in decomposing naturally occurring phosphates with sulphuric acid.

The process of forming superphosphate by the interaction of sulphuric acid with calcium fluorapatite is a multiphase, heterogeneous process which is usually diffusion limited. The process can be arbitrarily divided into two stages.

The first stage is diffusion of sulphuric acid to the apatite particles accompanied by a rapid chemical reaction on the particle surface which continues until the acid is completely consumed, and crystallization of calcium sulphate

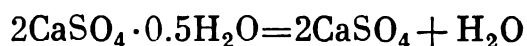


The second stage is diffusion of the phosphoric acid formed into the pores of the undecomposed apatite particles; it is accompanied by the reaction



The monocalcium phosphate formed is initially in solution, but it begins to crystallize out when the solution becomes supersaturated.

Reaction (a) ends in the superphosphate reaction chamber in 20 to 40 minutes, during the period of setting and hardening of the superphosphate pulp, which is caused by the relatively rapid crystallization of the low-solubility calcium sulphate and recrystallization of the hemihydrate to the anhydride by the reaction



The next stage of the process, ageing of the superphosphate, i.e. the formation and crystallization of monocalcium phosphate, is a slow one and it ends only at the storage site (final ageing), where the

superphosphate is kept from 6 to 25 days. The low rate of this stage is a result of the low rate of diffusion of the phosphoric acid through the crust of monocalcium phosphate formed on the surface of the apatite grains and of the extremely low rate of crystallization of the new solid phase  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ .

The optimal conditions for the reaction in the reaction den are determined not only by the kinetics of the reactions and the dif-

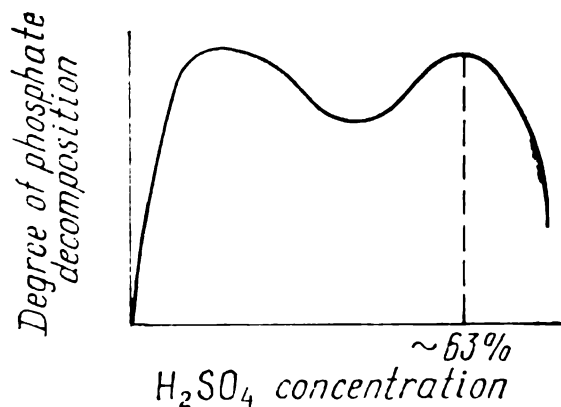


Fig. 29. Phosphate decomposition as a function of the concentration of the initial sulphuric acid

fusion of the acids, but by the structure of the calcium sulphate crystals formed, which effects the overall process rate and the quality of the superphosphate. The rates of diffusion and of reactions (a) and (b) can be raised by increasing the initial concentration of the sulphuric acid to an optimal value and by raising the temperature.

How the degree of decomposition of the phosphate raw material in a given time (isochrone) depends on the concentration of the initial sulphuric acid is shown in Fig. 29. The curve has two maxima. In the weak-solution region when the sulphuric acid concentration is raised, and in the high-concentration region when the concentration of the acid is lowered, the activity of the acid and, correspondingly, the degree of phosphate decomposition increase. However, with an increase in the activity of the acid supersaturation of the solution with respect to calcium sulphate grows; this is accompanied by rapid crystallization and formation of a dense  $\text{CaSO}_4 \times 0.5\text{H}_2\text{O}$  crust on the surface of the apatite particles, which retards diffusion of the phosphoric acid. Due to these phenomena there is a range of sulphuric acid concentrations where the rate and degree of phosphate decompositions drop; this corresponds to the minimum of the curve in Fig. 29.

The location and the values of the maxima of the curve depend on the nature of the raw material used, the S : L ratio of the pulp, temperature, residence time of the pulp in the reactor, etc. In industrial conditions an acid concentration which corresponds closely to the second maximum of Fig. 29 is used. The range of optimal sulphuric acid concentrations for the industrial process lies within the limits 62-69%; in the continuous process for making superphosphate the initial sulphuric acid concentration is 68-69.5%. At this concentration of the acid the temperature in the reaction den is approximately 110-115 °C; the rise in the temperature is a result of the heat liberated in exothermic reactions (a) and (b). In these

conditions a friable, porous layer of calcium sulphate is formed on the phosphate particles, and diffusion of phosphoric acid into the particles takes place at a fairly high rate.

Ageing (or curing) is the slowest stage of the production process. The ageing rate can be increased by cooling the superphosphate and by evaporating water from it, which promotes crystallization of monocalcium phosphate and increases the rate of reaction (b) by raising the phosphoric acid concentration of the solution. To accomplish this the superphosphate is agitated and scattered during storage.

The  $P_2O_5$ -content of the end product is about half that of the raw material and amounts to 19-20%  $P_2O_5$  for superphosphate made from apatite and 14% for superphosphate from phosphate rock.

The end product still contains a certain amount of uncombined phosphoric acid, which makes the fertilizer more hygroscopic. Neutralizing admixtures are used to remove the free acid of the superphosphate, or it is treated with gaseous ammonia. These procedures improve the physical properties of the superphosphate; they lower the moisture content, the hygroscopicity and the tendency to cake. If ammonia treatment is used, an additional nutritional component (nitrogen) is also introduced into the fertilizer.

Batch, semicontinuous and continuous processes are used for manufacturing superphosphate. Only a few plants still use batch-operation dens. These have all the typical faults of batchwise operations: they are of low production capacity, costs are high, the composition and properties of the product are not constant, the air in the plant is contaminated with the gases and dust from the process, etc. At present all new plants are designed to employ a continuous-operation method and most older plants are being reconverted to such a method.

The flow diagram of a continuous-operation process for making superphosphate is given in Fig. 30. Ground apatite concentrate (or phosphate powder) by a system of belt- and screw conveyors and elevators is transported from the storage site to automatic weigh-feeder, which feeds it to a continuous-action mixer.

The sulphuric acid (75%, tower  $H_2SO_4$ ) is continuously diluted with water in a batch feeder-mixer to a 68%  $H_2SO_4$  concentration, measured by a concentration meter, and is then fed to the mixer, where the phosphate raw material and the sulphuric acid are agitated mechanically. The pulp formed is transformed from the mixer to the continuous-action reaction den, where formation of the superphosphate (setting and hardening of the pulp in the first stage of ageing of the superphosphate) takes place. The superphosphate powder from the den is transferred for ageing by a conveyer belt located below the den to the superphosphate storage site, where it is uniformly distributed by a scattering device. To accelerate ageing

the superphosphate is agitated during storage by means of a grab-bucket crane.

Superphosphate is granulated in revolving drum granulators to improve its physical properties. In the granulator the powder-form superphosphate is wetted with water fed into the drum through nozzles, and rolled into granules of different size which are then dried, separated into size fractions and weighed into paper bags.

During decomposition of the phosphates with sulphuric acid in the den, hydrogen fluoride evolved reacts with the silica contained in the phosphates and forms gaseous silicofluoride,  $\text{SiF}_4$ , and

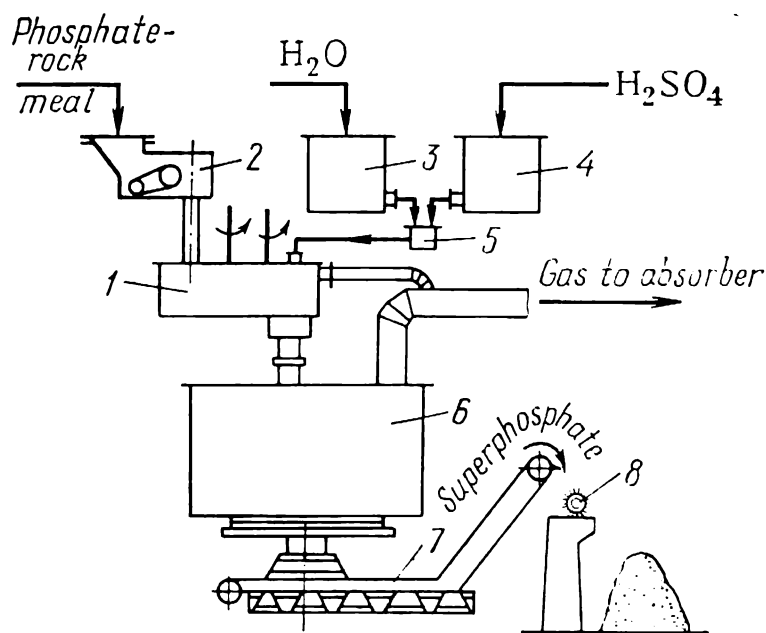


Fig. 30. Flow diagram of the continuous superphosphate-manufacturing process:

1—mixer; 2—phosphate weigh-feeder; 3, 4—head tanks for sulphuric acid and water; 5—acid measuring device; 6—superphosphate den; 7—superphosphate conveyor; 8—superphosphate scatterer at the storage site

hydrosilicofluoric acid,  $\text{H}_2\text{SiF}_6$ . The fluorous gases, containing  $\text{H}_2\text{SiF}_6$  vapours, are withdrawn through an opening in the den roof and a ventilation pipe to an absorption unit and are utilized for making sodium fluo-silicate.

The principal piece of apparatus in the manufacture of superphosphate is the superphosphate den. The mixer from which the pulp is fed to it is located directly on the den top. Mixers of a screw-conveyor type or of a chamber type with mechanical agitator are employed to provide continuous feed of the mix to the superphosphate den. Depending on the size of the chamber, one or two agitators are used.

The most common type of continuous-action superphosphate dens is a cylindrical revolving chamber of the kind shown schematically in Fig. 31. It is a vertical, reinforced-concrete cylinder, covered with sheet metal and with an inner lining of acid-resistant diabase blocks. The cylinder together with the reinforced-concrete bottom revolves

slowly on roller supports about a stationary, hollow cast-iron tube, which passes up through a seal in the den bottom and serves for removing the superphosphate from the den. The stationary, reinforced-concrete top of the den rests on supports. The vertical partition which separates the feed zone from the discharge zone is suspended from the chamber top. Superphosphate slurry is continuously introduced into the den from the mixer through a hatch in the den top. The cutter located in the discharge zone near the partition rotates in the direction opposite to that of the den motion. The den makes one complete revolution in 1.5 to 2.5 hours. During that period the superphosphate slurry solidifies and ageing begins. Superphosphate in condition to be discharged is shaved off the solid block by the cutter blades and the shavings fall through the hollow central tube onto a conveyer belt for transferring the superphosphate to the storehouse.

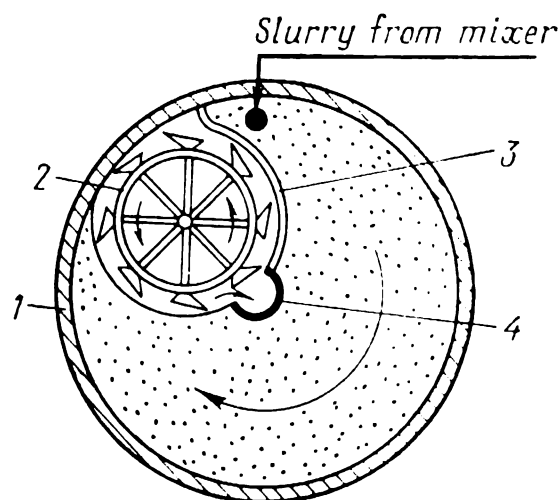


Fig. 31. Continuous-action superphosphate den:

1—rotating shell; 2—cutter; 3—partition;  
4—stationary discharge pipe

The production capacity of a den 7.1 m in diameter and 2.5 m high amounts to 30-50 tons of superphosphate per hour and its operation intensity lies between 550 and 650 kg per cu m.

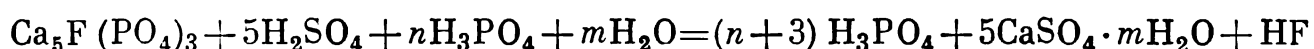
A negative feature of simple superphosphate is its comparatively low content of the nutrient—not over 20%  $P_2O_5$  when made from apatite concentrates, and 15%  $P_2O_5$  when made from phosphate rock. More highly concentrated phosphatic fertilizers can be obtained by decomposing the phosphate ores with phosphoric acid.

**The manufacture of wet-process phosphoric acid and triple superphosphate.** Phosphoric acid is an intermediate product used in manufacturing triple superphosphate, mixed concentrated fertilizers and other phosphatic compounds. Phosphoric acid is made both by electrothermal methods and by extraction processes, i.e. by winning  $H_3PO_4$  from naturally occurring phosphates with acids.

The sulphuric-acid process is the one most commonly used for manufacturing technical grade, wet-process phosphoric acid. The method consists in treating naturally occurring crushed phosphates with an excess of sulphuric acid to produce phosphoric acid and solid phase phosphogypsum—calcium sulphate which contains a remainder of undecomposed phosphate.

Sulphuric acid is mixed with the phosphate to form a slurry with an L : S ratio of between 2.5 : 1 and 3.5 : 1. The necessary ratio is maintained by diluting the sulphuric acid with a mixture of the

phosphoric acid product and the wash water from the phosphogypsum-washing operation. It follows that extraction is carried out with a mixture of phosphoric and sulphuric acids, and the overall reaction can be expressed as follows:



The solution of phosphoric acid obtained by filtering off the phosphogypsum contains impurities introduced with the phosphate—silica, sulphates and phosphates of iron and aluminium, etc.

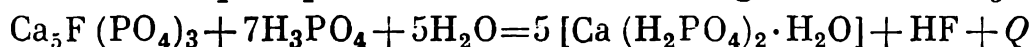
Optimal conditions for the extraction process provide maximum acid concentration, large-size phosphogypsum crystals, and as a result good filtering, and a high leaching rate. The rate at which the phosphate dissolves is controlled by the diffusion of hydrogen ions to the surface of the phosphate particles or of calcium ions to the core of the solution. At high concentrations the viscosity of the phosphoric acid solution is also higher and this lowers the rate of diffusion and, consequently, of dissolution. Large phosphogypsum crystals are formed at a temperature of 70-80 °C and at low sulphuric acid concentrations. To obtain phosphoric acid of higher strength and to increase the process rate, 75%-concentration tower sulphuric acid (and in some cases even vitriol oil) is used and temperatures in the early stages of extraction are maintained at higher level. The extraction rate is also increased by means of intensive stirring. The process is a continuous one, carried out in a battery of reactors with agitators, i.e. in a cascade of extractors interconnected by overflow pipes. The phosphogypsum is removed in continuous-action rotary-drum vacuum filters and then washed a number of times with water and dilute recycled solutions. The phosphogypsum contains a certain amount of phosphorus and can be utilized as an indirect fertilizer for improving soil structure, or as a direct fertilizer for some crops, and also as a building material.

Phosphoric acid obtained by the wet method does not usually contain over 36%  $\text{H}_3\text{PO}_4$ . For use in manufacturing triple superphosphate and other fertilizers the acid must be evaporated to a higher concentration (50-80%  $\text{H}_3\text{PO}_4$ ). Concentration of phosphoric acid is complicated by corrosion of the equipment and by precipitation of calcium sulphate and other impurities on the heating surfaces. Because of this, the most often used are drum concentrators, in which heating occurs by direct contact of the gaseous combustion products with the acid, in the same fashion as in sulphuric-acid concentration.

The electrothermal method of making phosphoric acid is based on reduction of the phosphorus in calcium phosphate at high temperatures (1400-1600 °C) in electric furnaces. The phosphorus vapour in the furnace effluent is oxidized (burned) to form phosphorus pentoxide, which is hydrated to produce phosphoric acid (the so-

called thermal phosphoric acid). The principal advantages of the electrothermal process as compared to extraction are the possibility of making phosphoric acid of any desired concentration (up to 100%  $\text{H}_3\text{PO}_4$ ) and the high degree of purity of the product; moreover, any phosphates, including low quality ones not subjected to beneficiation, can be used as raw materials. However, the electric energy-consumption indexes are very high: they are considerably higher than for manufacturing phosphoric acid by the extraction method.

Triple superphosphate is made by decomposing naturally occurring phosphates with phosphoric acid containing 70-80%  $\text{H}_3\text{PO}_4$ :



Triple superphosphate, in contrast to simple superphosphate, consists mainly of monocalcium phosphate and is a concentrated fertilizer, containing 40-50%  $\text{P}_2\text{O}_5$ , i.e. 2 to 3 times more than simple superphosphate. The equipment used for manufacturing triple superphosphate is similar to that used in making simple superphosphate, i.e. various types of mixers for contacting the phosphoric acid with the phosphate raw material and continuous-action dens. In some manufacturing schemas the solidification of the pulp discharged from the mixer takes place on a belt conveyer, which moves the product to the storage site. In so-called no-den schemas pulp from the mixer is transferred directly to granulators and dryers and the granulated product does not require ageing.

Sulphuric-acid decomposition of phosphates produces a simple fertilizer as the end product. Nitric-acid decomposition of phosphates gives an extract containing calcium, nitrogen and phosphorus, which can be converted into concentrated and complex fertilizers; for instance if potassium salts are added, a three-component, nitrogenous-potash-phosphatic fertilizer is produced.

## 5. Nitrogenous Fertilizers

Most nitrogenous fertilizers are synthetic products obtained by neutralizing acids with alkalis. The initial materials used in making nitrogenous fertilizers are sulphuric and nitric acids, carbon dioxide, liquid or gaseous ammonia, calcium hydroxide, and some others. The nitrogen is contained in the fertilizers either in an  $\text{NH}_4^+$ -cation, i.e. in the ammonium form, as  $\text{NH}_2$  (amide) or in an  $\text{NO}_3^-$ -anion, i.e. in the nitrate form; some fertilizers contain both ammonium and nitrate forms of nitrogen. All nitrogenous fertilizers are soluble in water and are readily available to plants, but they are easily carried away into the deeper layers of the soil if there is an excess of rain or irrigation. One of the most common nitrogenous fertilizers is ammonium nitrate.

**The manufacture of ammonium nitrate.** Ammonium nitrate is a fertilizer which contains no ballast and which has a 35% content



of nitrogen in the ammonium and nitrate forms and it can therefore be used with advantage on soils of all types and for all kinds of crops. However, the fertilizer has unfavourable physical properties. Ammonium-nitrate crystals "melt" when exposed to air or cake into large aggregates due to the hygroscopicity, high solubility

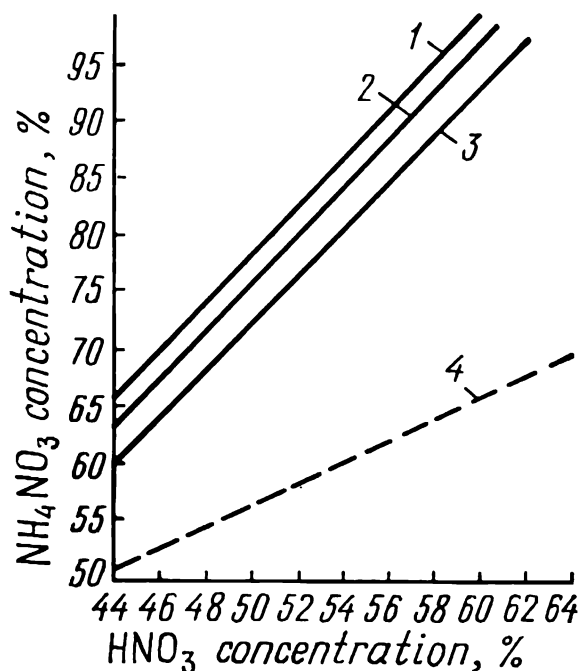


Fig. 32. Concentration of  $\text{NH}_4\text{NO}_3$  solutions vs nitric acid concentrations at various temperatures:

1—70 °C; 2—50 °C; 3—20 °C; 4—without utilization of heat of the reaction

in water and large temperature coefficient of solution of the material. Moreover, temperature changes during storage can result in a changeover from one crystalline form to another, i.e. in recrystallization, and this also leads to caking. To decrease the caking, the ammonium nitrate particles are powdered using finely ground low-hygroscopicity substances—limestone, phosphate-rock or bone meal, gypsum or kaolin, or are granulated together with admixtures of nitrates of calcium and magnesium or calcium phosphates. At present, ammonium nitrate for use as a fertilizer is manufactured exclusively in the form of granules. It has recently been established that some bacteria denitrogenize ammonium nitrate and convert it into a compound

useless for the soil (down to elemental nitrogen) and, moreover, this is accompanied by depletion of the organic content of the soil. This is an additional drawback of ammonium nitrate when used as a fertilizer.

The danger of fire and explosions complicates the manufacture of ammonium nitrate and its use as a fertilizer.<sup>1</sup>

Ammonium nitrate is produced at plants where synthetic ammonia and nitric acid are manufactured. It is made by neutralizing weak nitric acid with gaseous ammonia, evaporating the solution obtained and prilling the ammonium nitrate.

The neutralization stage is based on the reaction



This chemisorption process, in which the absorption of the gas by the liquid is accompanied by a rapid chemical reaction, is diffusion controlled and highly exothermic. The heat of neutralization is utilized in evaporating water from the ammonium-nitrate solutions. From Fig. 32 it is evident that by using high-strength nitric

acid and heating the starting reagents, molten ammonium nitrate (concentrations higher than 95-96%  $\text{NH}_4\text{NO}_3$ ) can be obtained directly, without evaporating the solution.

At the present time, the most extensively used schema is one in which the solution is partially concentrated by evaporation at the expense of the heat of neutralization (Fig. 33). The main part of the water is removed in a UHN (utilizer of the heat of neutralization)

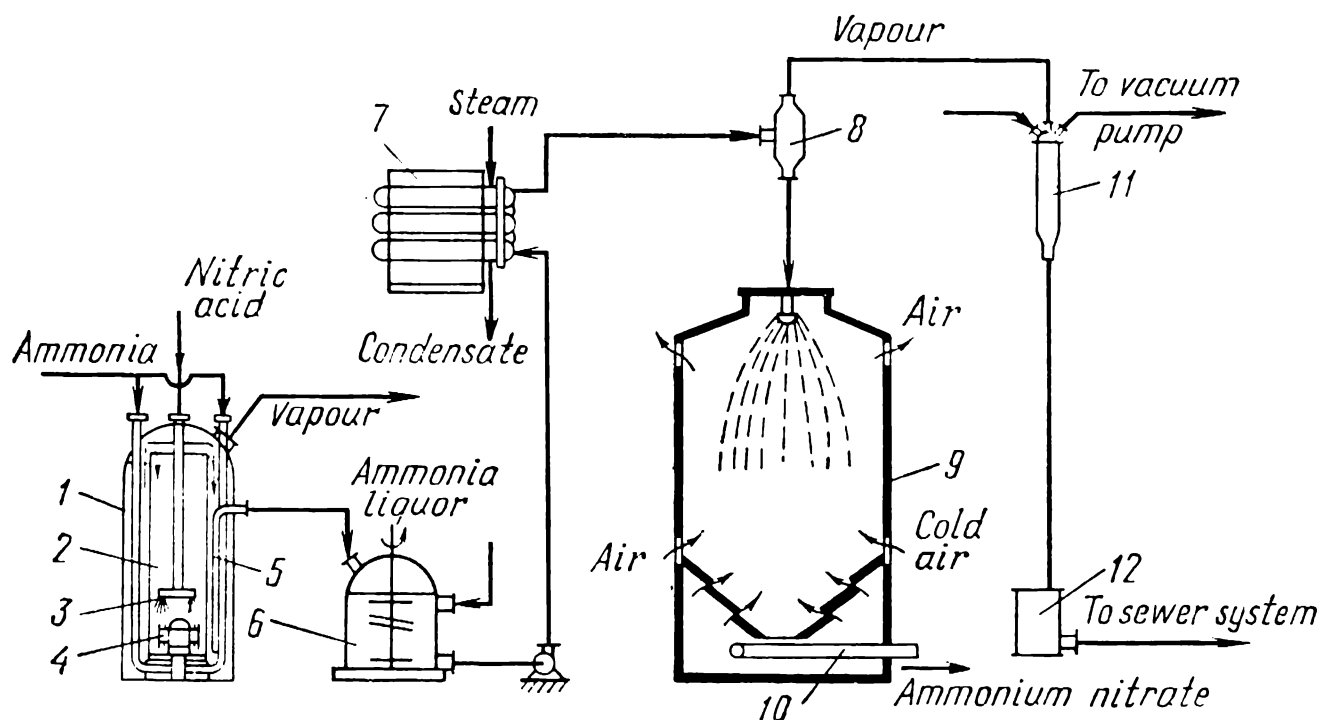


Fig. 33. Flow diagram of process for making ammonium nitrate employing a UHN reactor and evaporation of the solution:

1—neutralizer shell; 2—inner cylinder; 3—nitric-acid distributor; 4—ammonia feeder; 5—hydraulic seal; 6—final neutralizer; 7—second-stage vacuum-evaporation unit; 8—separator; 9—prilling tower; 10—ammonium-nitrate conveyer; 11—barometric condenser; 12—barometric-condenser seal

neutralizer. This apparatus (Fig. 33) consists of a cylindrical vessel made of stainless steel with a second cylinder inside it. Gaseous ammonia and nitric acid are continuously fed to the cylinder; the nitric acid is introduced through a sprayer nozzle. The reactants move through the neutralizer in cocurrent flow. The inner space of the cylinder is the neutralizing part of the apparatus, and the annular space between the inner and outer cylinders is for evaporation. Heat is removed from the reaction zone through the wall of the inner cylinder. The solution of ammonium nitrate formed flows over the upper rim of the cylinder into the evaporator part, where water is evaporated as a result of heat transfer from the neutralization part of apparatus to the evaporation part. Heat must be removed from the neutralization zone not only to evaporate the solution, but also to avoid overheating, which leads to decomposition of nitric acid and ammonium nitrate.

The vapour is withdrawn from the neutralizer and is utilized as a heating agent. The ammonium nitrate solution (60 to 80%  $\text{NH}_4\text{NO}_3$ , depending on the concentration of the nitric acid used) flows to a vessel with an agitator—the final neutralizer—through a hydraulic seal and then to a multistage vacuum-evaporation unit. In the final neutralizer the weakly acidic solution is subjected to an additional stage of neutralization with ammonia; admixtures for preventing fertilizer caking are usually also introduced in this apparatus.

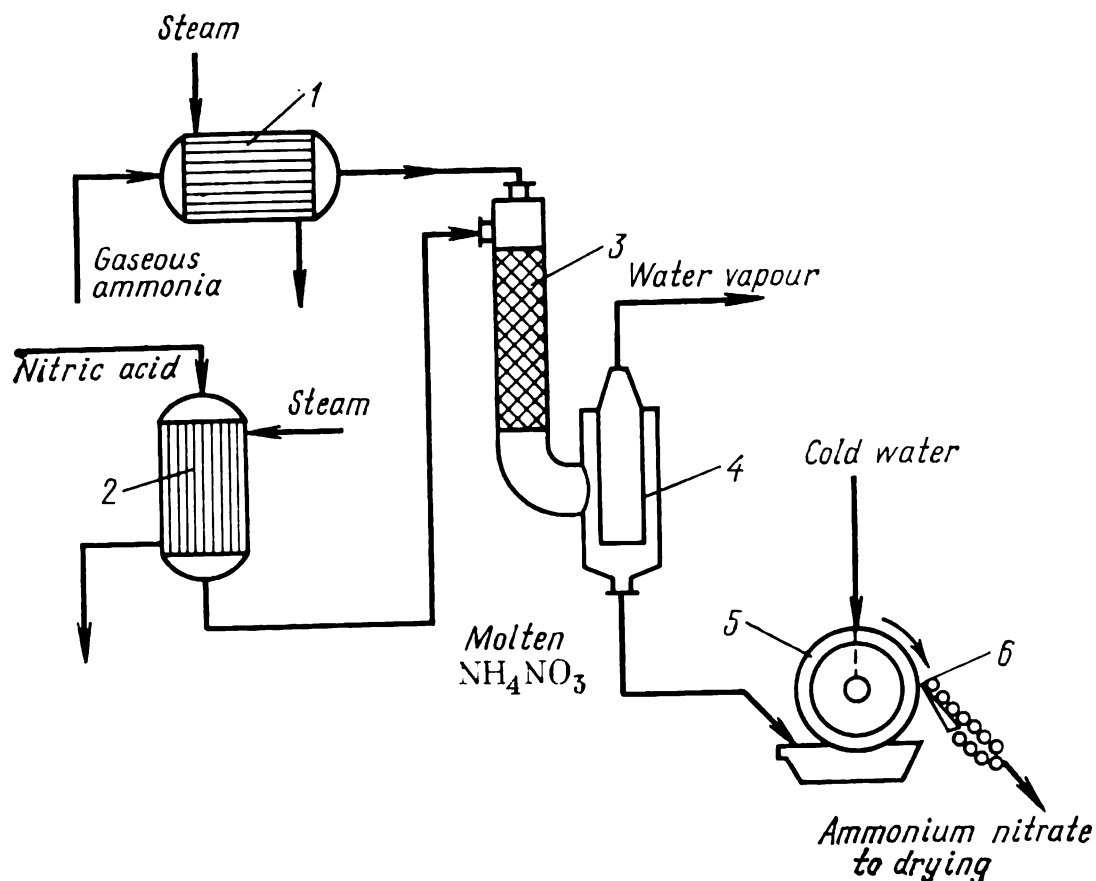


Fig. 34. Flow diagram of ammonium nitrate no-evaporation manufacturing process:

1—ammonia heater; 2—nitric-acid heater; 3—reactor; 4—separator; 5—drum crystallizer; 6—knife

Two or three stages of evaporation are used, with the vapour from the UHN together with vapour from the evaporators and fresh saturated steam as the heating agents. In the evaporation units the concentration is brought up to 98-99%  $\text{NH}_4\text{NO}_3$  and the ammonium nitrate melt obtained is transferred first to a separator and then to a prilling tower. Granulation is accomplished by spraying the molten mass down through a hollow reinforced-concrete tower, 30-35 m high. The spray is formed by feeding the molten mass through a rotating perforated funnel or onto a rotating horizontal disc. In their path down through the tower the drops of the molten mass solidify into granules when they are cooled by the air forced up through the tower countercurrent to the drops by fans; the gra-

nules drop onto a conveyer belt, which transports the product to the drying and packing sections.

Some plants produce ammonium nitrate in the form of crystalline aggregates (flakes) instead of granules, by crystallizing the melt on the surface of a rotary drum cooled from the inside with water (Fig. 34).

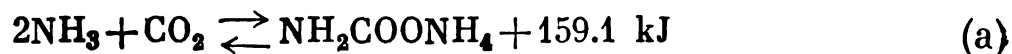
The no-evaporation, single-stage method of manufacturing ammonium nitrate is based on a rapid reaction under a pressure of 4 atm between ammonia and 60% nitric acid, preheated in interchangers. The vapour-liquid emulsion leaving the reactor is separated into its composite parts in a separator and the 97-98%  $\text{NH}_4\text{NO}_3$  melt is transferred to a granulator. A simplified flow diagram of ammonium nitrate production by the no-evaporation method is given in Fig. 34.

Due to the negative features of ammonium nitrate mentioned above, it is best to use it as the basis for making complex and mixed fertilizers. Calcium-ammonium nitrate, ammonium sulphate-nitrate, etc. are made by mixing ammonium nitrate with limestone and with ammonium sulphate. Nitrogenous-potash-phosphatic fertilizers can be made by melting  $\text{NH}_4\text{NO}_3$  with salts of phosphorus and potassium. Ammonium nitrate is also used for making liquid fertilizers, by dissolving it in liquid ammonia or ammonia liquor.

**The manufacture of urea.** Urea (carbamide) is a high-quality nitrogenous fertilizer with a 46% nitrogen content. Urea is also used as a nitrogen-containing admixture to animal foods. Urea is not only extensively employed in agriculture; it has many uses in industry as well. It is used in making urea resins from which in turn high-quality plastics (aminoplast), chip board, synthetic glues, compositions for impregnating cloth, etc. are made. Urea is also widely employed in the pharmaceuticals industry and in manufacturing synthetic fibres.

Urea is synthesized from ammonia and carbon dioxide. The manufacturing process consists of the following stages: chemical reaction between  $\text{NH}_3$  and  $\text{CO}_2$  (synthesis), distillation of the synthesis products, and processing the urea solutions obtained in the distillation operation into the end product.

Synthesis itself consists of two stages, in the first ammonium carbamate (carbamate) is formed:



The second stage is dehydration of the carbamate to produce liquid-phase urea (melt)



The overall process by which urea is formed is a G-L heterogeneous, kinetics-limited one, with the rate determined by that of dehydration of ammonium carbamate in the melt, the slowest stage.

The equilibrium ratios and rate of urea synthesis depend on the pressure, temperature and chemical composition of the system. Since the vapour pressure of the ammonium carbamate is very

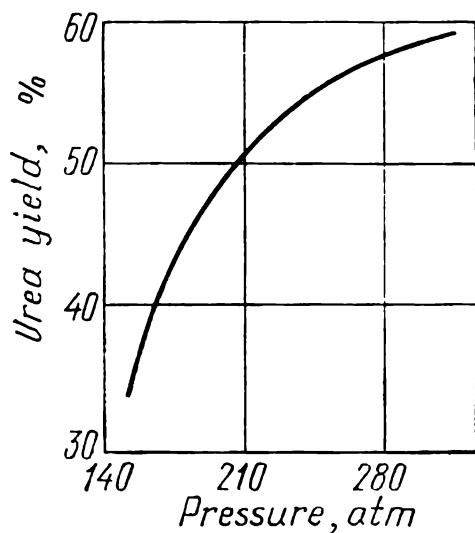


Fig. 35. Urea yield vs process pressure

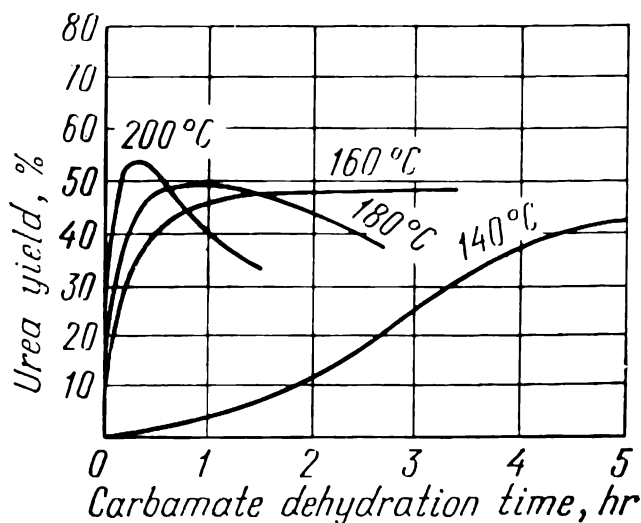


Fig. 36. Dependence of urea yield on the temperature and residence time of the reaction mixture in the reactor

high and, moreover, the overall result of the synthesis reaction is a decrease in the gas volume, the equilibrium urea yield grows with pressure. The process rate and actual urea yield also grow rapidly with the pressure, due to the increased process driving force, i.e. the concentrations of the gas-phase reactants (Fig. 35).

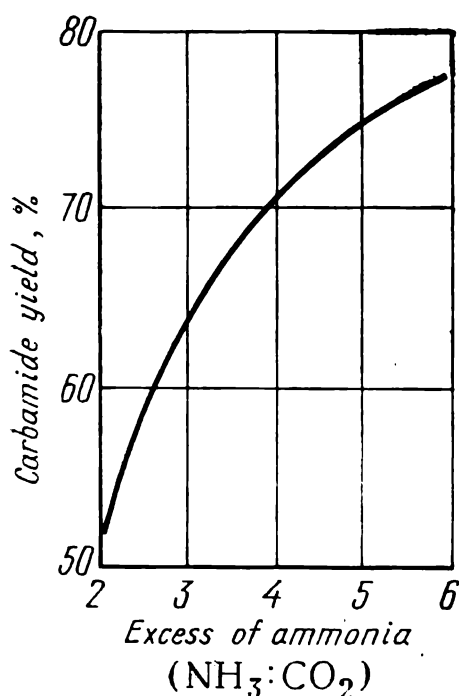


Fig. 37. Equilibrium carbamide yield as a function of excess ammonia

The rate of the process and in particular that of the limiting stage (b) rise sharply with the temperature and the result is an increase in the actual urea yield (Fig. 36). Fig. 36 shows that at above 180°C the yield curve has a maximum. If the residence time of the reaction mixture in the heated zone is increased further the urea yield drops as a result of the speed up of side reactions. The product yield can also be raised by employing an excess of ammonia in the initial mixture over the stoichiometric ratio

(Fig. 37). An excess of ammonia impedes formation of side products of carbamate hydrolysis and shifts the equilibrium of stage (b) towards formation of urea, since the excess combines with water for-

med by dehydration of the ammonium carbamate. The excess ammonia in the reaction mixture also reduces apparatus corrosion.

In industry urea synthesis is carried out without using a catalyst, at pressures of 180-200 atm and temperatures of 180 to 200 °C. Higher temperatures cannot be used, mainly because they increase corrosion of the apparatus. The raw materials are the expansion

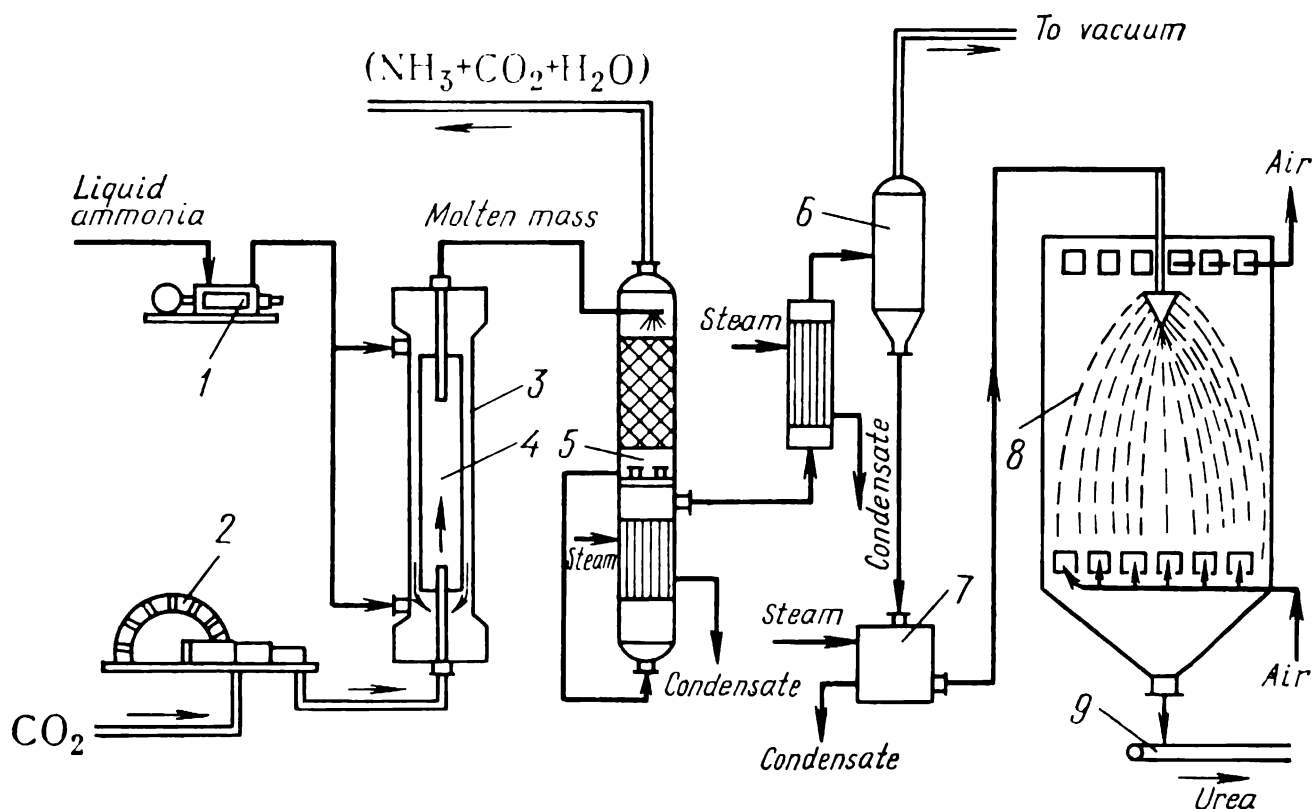


Fig. 38. Flow diagram of urea-production process:

1—pump; 2—compressor; 3—synthesis tower; 4—inner cup (reaction chamber); 5—distillation tower; 6—evaporator; 7—tank for the molten mass; 8—prilling tower; 9—conveyor

gas obtained in the process of manufacturing ammonia (contains up to 90%  $\text{CO}_2$ ) and liquid ammonia, used in a 100-125% excess over the stoichiometric amount.

Under these conditions the urea yield (with respect to  $\text{CO}_2$ ) lies between 60 and 70%, and the molten mass obtained by dehydration of the carbamate contains approximately 35% urea. Good economics of the process and low cost of the urea can only be achieved by utilizing the part of the reactants—ammonia and carbon dioxide—which do not enter into the reaction.

A simplified flow diagram of an urea-manufacturing plant is given in Fig. 38. Synthesis takes place in a tower made of alloy steel; the inner cylinder of the tower serves to protect the walls of the high-pressure vessel against corrosion by the reaction mixture. Liquid ammonia is fed to the annular space between the tower wall and the inner cylinder by a pump; it flows along the walls, protecting them from corrosion. The ammonia reacts with the carbon dioxide which is fed to the inside of the cylinder at the tower bottom. The

tower operates in plug flow. The molten urea is removed from the upper part of the tower, throttled to atmospheric pressure and transferred to a distillation tower, where the excess ammonia and products of the decomposition of ammonium-carbonate salts are stripped from the urea solution. The solution is concentrated in an evaporator and the urea is produced in the form of either crystals or it is granulated in a prilling tower.

The gases discharged from the distillation tower are regenerated. The various processes for manufacturing urea differ in the methods used to separate and regenerate these gases: they may be utilized in a neighbouring unit for manufacturing ammonium nitrate, may be separated by selective absorption of  $\text{CO}_2$  or of  $\text{NH}_3$  with one of a number of different sorbents, both reagents being returned to the process (gas phase recycle), or may be utilized by absorbing both  $\text{NH}_3$  and  $\text{CO}_2$  from the gas with an inert mineral oil to form a suspension of ammonium carbamate in the oil which is recycled to the synthesis tower, by returning  $\text{NH}_3$  and  $\text{CO}_2$  to the processing cycle in the form of aqueous solutions of ammonium salts (liquid-phase recycle), etc.

## 6. Soda

Sodium alkalies, commercially known as soda products, are produced and consumed in tremendous amounts. Soda products include soda ash (sodium carbonate),  $\text{Na}_2\text{CO}_3$ ; bicarbonate, or sodium bicarbonate,  $\text{NaHCO}_3$ ; sal soda,  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ; sodium carbonate monohydrate (heavy ash),  $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ , and caustic soda (sodium hydroxide),  $\text{NaOH}$ .

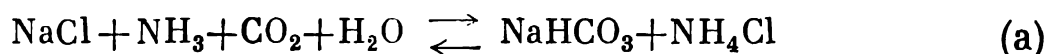
Soda ash, which is one of the most important of all chemical products and is a starting material in producing many other chemicals, is produced in the largest amounts compared with other soda products. Sodium carbonate is a white, crystalline powder with a density of  $2.53 \text{ g/cm}^3$ , melting point of  $853^\circ\text{C}$ , bulk density of about  $0.5 \text{ t/m}^3$ . Aqueous solutions of soda are strongly alkaline due to hydrolysis of the  $\text{Na}_2\text{CO}_3$ . Soda ash is used in the inorganic chemicals industry for producing other soda products and a number of inorganic salts, in metallurgy, in the glass industry, for petroleum-products purification, in the pulp-and-paper, paint-and-varnish, textile, leather and many other branches of industry. The principal consumers of the stronger base, sodium hydroxide, are the aluminium, petroleum-refining, pulp-and-paper, soap, paint-and-varnish branches of industry, the synthetic fibre and organic-synthesis industries, etc.

Soda ash is a salt of a strong base and a weak acid. The manufacture of this multitonnage chemical product is an example of large-scale salt production processes based on chemisorption reactions in a gas-liquid system.

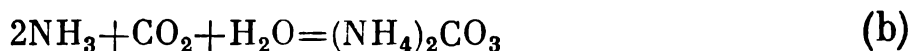
**The ammonia method for manufacturing soda** is the chief method now in commercial use. The basic principles of the process were developed at the end of the 19th century by Solvay, a Belgian engineer, and the theory of the process was developed by the Russian scientist P. P. Fedotiev, and then by other Soviet scientists.

*The raw materials* for manufacturing soda are limestone or chalk, common salt in saturated solutions, and ammonia.

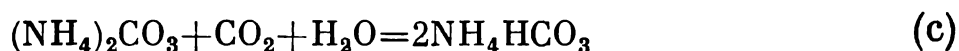
The chemical reactions which take place in the various stages of the ammonia-soda process are described by the overall equation:



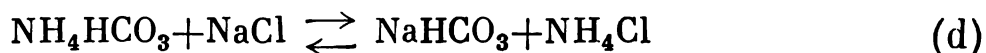
This reaction consists of several separate stages which take place when a saturated NaCl solution reacts consecutively with ammonia (ammoniation) and with carbon dioxide (carbonation). The stages of overall reaction (a) can be described by the simplified equations of monocarbonation,



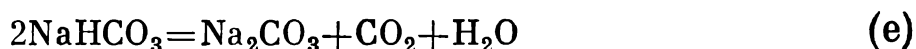
bicarbonation,



and exchange decomposition



The brine must be ammoniated for introduction of carbon dioxide, which is insoluble in a saturated NaCl-solution. Absorption of  $\text{CO}_2$  by the ammoniated brine results from chemical reaction of the  $\text{CO}_2$  with the dissolved ammonia (chemisorption). Reaction (d) is the basic operation in the ammonia-soda process and the yield of the product, sodium bicarbonate, depends on the reaction equilibrium. The least soluble compounds, sodium bicarbonate, precipitates out, is filtered off and calcined. This last operation produces the end product, soda ash, and carbon dioxide, utilized in carbonation



In this way part of the carbon dioxide used in the process is regenerated. The carbon dioxide deficiency is covered with  $\text{CO}_2$  obtained by calcining limestone



The lime formed in the calcination process is used for preparing milk of lime



The milk of lime is needed for regenerating the ammonia from the mother liquor (filtrate) obtained in separating the bicarbonate from



solution. Regeneration is carried out by distilling the filtrate together with milk of lime



The regenerated ammonia is used for ammoniating the salt brine, whereas the calcium chloride solution is a waste product of the soda-manufacturing process.

Production of soda ash is carried out at two main production sections: at the soda-ash section and at the lime-kiln section, which usually supplies its product to other sections at a large chemical works besides the soda-ash section.

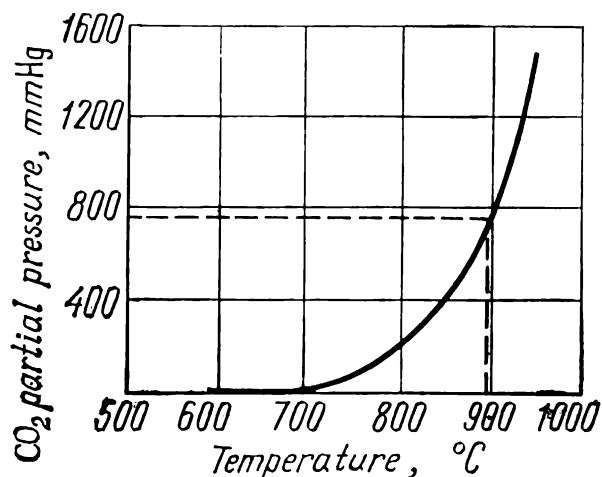


Fig. 39. Equilibrium  $\text{CO}_2$ -pressure vs temperature for calcium-carbonate dissociation

*Lime-kiln sections* are not only needed at soda works but also in many other industries where one of the raw materials is lime or carbon dioxide. Such sections are employed in producing chlorinated lime, calcium nitrate, calcium carbide, building materials, etc.

The limestone-dissociation reaction, (f), is reversible and endothermic. The heat necessary for dissociation is supplied by burning coal introduced into the kiln together with the limestone.

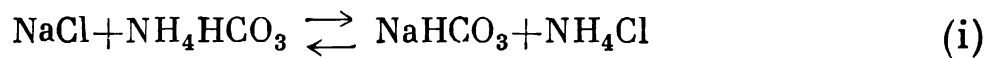
The basic factor governing both the equilibrium and the rate of dissociation is the process temperature. The equilibrium carbon-dioxide vapour pressure (the  $\text{CaCO}_3$ -dissociation pressure) which determines the value of the equilibrium constant of the process reaches 1 atm at a temperature of 989 °C (Fig. 39). The dissociation rate can be increased by raising the temperature and reducing the lump size of the limestone and fuel to an optimal value to develop the phase interface (G-S). If the size of the limestone and coal lumps is too small, the pressure drop across the charge increases and this leads to sintering. Raising the temperature above 1200 °C results in formation of low-melting silicates and ferrites of calcium, and the lumps of the charge stick together and form large aggregates which disrupt normal kiln operation.

Limestone is calcined in air-blast, shaft furnaces with temperatures in the calcination zone of 1100-1200 °C and lump sizes of the limestone from 40 to 120 mm and of the coal from 40 to 80 mm. The carbon dioxide content of the kiln gas does not exceed 40% since the carbon dioxide formed by limestone dissociation is diluted with the weak gas produced by the burning of coal in the air blast. Considerably more carbon dioxide is obtained in the kilns, along

with the lime necessary for ammonia regeneration, than is required for making up the losses of  $\text{CO}_2$  in the ammonia-soda process. Therefore, part of the kiln gas is utilized for other purposes or is simply discharged to the atmosphere. Milk of lime is produced by slaking the lime with water and weak, recycled solutions in rotary drum-slakers. Large-size particles of undecomposed limestone and other impurities are removed from the milk of lime in a perforated drum, and small particles—in classifiers or hydrocyclones. The  $\text{Ca}(\text{OH})_2$  content of the milk-of-lime suspension is from 270 to 308 g/l, depending on the quality of the lime and the slaking conditions.

*The physicochemical principles underlying carbonation of ammonia-salt solutions* are very complex. The most important in the soda-manufacturing process is the operation of carbonation of the ammoniated brine. Sodium bicarbonate is formed during carbonation by complex chemical processes. Carbonation of the ammoniated brine is accompanied by ion reactions between the dissolved substances, which are in dynamic equilibrium with undissociated molecules of the precipitated  $\text{NaHCO}_3$  and with the gas.

The principal process occurring during carbonation-precipitation of sodium bicarbonate can be expressed by the equation



The equilibrium of reaction (i) and the  $\text{NaHCO}_3$  yield depend on the solubilities of the salts in this complex system, which was first studied by Fedotiev.

A four-sided diagram of the 15 °C isotherm for this system (projection of the spatial diagram on a plane) is given in Fig. 40a. In this diagram the solubility of each of the pure salts of the system is represented by one of the corners of the square and salts with a common ion (for instance  $\text{NaHCO}_3$  and  $\text{NaCl}$  or  $\text{NaCl}$  and  $\text{NH}_4\text{Cl}$ ) are at neighbouring corners.

The double eutonic points *I*, *II*, *III* and *IV*, which correspond to solutions saturated with two salts, are located on the sides of the square, and the triple points  $P_1$  and  $P_2$  are inside the square. Point  $P_1$  corresponds to a solution containing  $\text{NaHCO}_3$ ,  $\text{NH}_4\text{HCO}_3$  and  $\text{NaCl}$  in equilibrium with the solid salts— $\text{NaHCO}_3$ ,  $\text{NH}_4\text{HCO}_3$  and  $\text{NH}_4\text{Cl}$ , whose fields of crystallization meet at that point. At point  $P_2$  the liquid and solid phases of the saturated solution have the same composition ( $\text{NaCl}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NaHCO}_3$ ). The lines inside the square which connect the eutonic points are lines of simultaneous precipitation of the two salts whose fields of crystallization are in contact with each other. It is evident from Fig. 40 that the least soluble substance of this system is  $\text{NaHCO}_3$ , whose crystallization field (area  $1\text{—}IV\text{—}P_1\text{—}P_2\text{—}I$ ) occupies more than 2/3 of the area of the diagram.

The four-sided diagram gives only the composition of the anhydrous salts (the dry remainder of the saturated solutions); the ion concentrations are expressed in per cent, i.e. the sum of both cations,  $\text{Na}^+ + \text{NH}_4^+$ , equal to the sum of the anions,  $\text{Cl}^- + \text{HCO}_3^-$  in gram equivalents is always unity (or 100%). If the ion composition of the

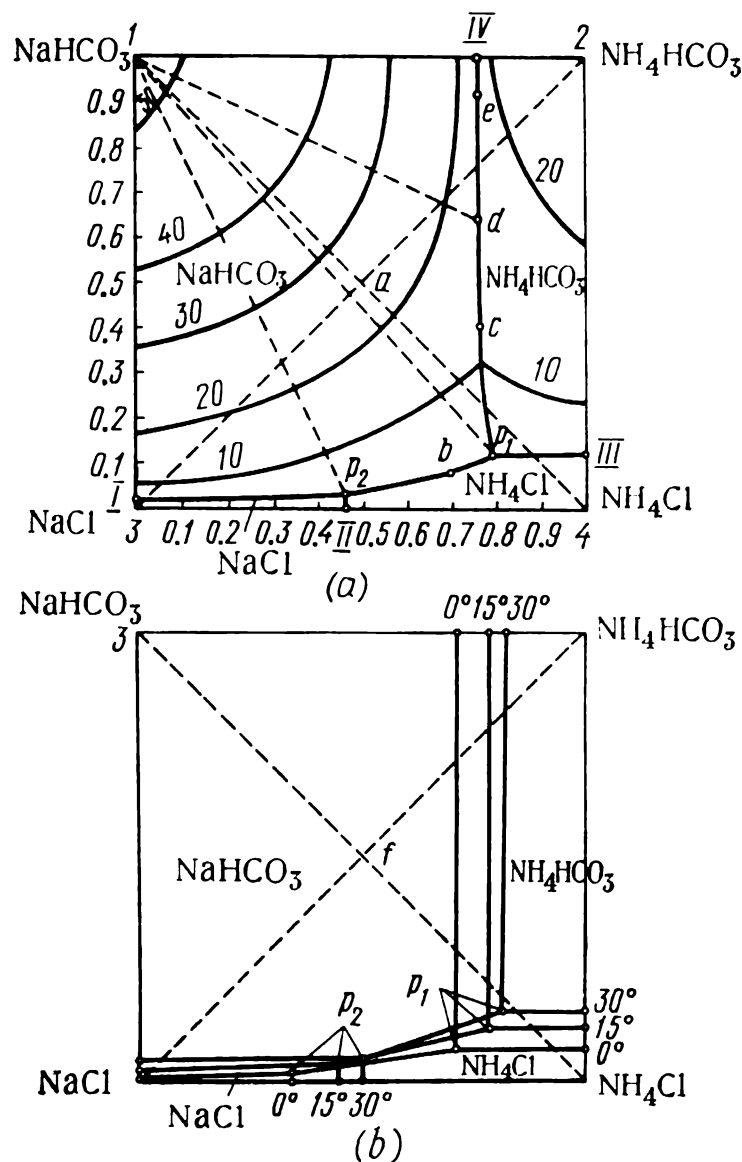


Fig. 40. Solubility diagram of  $\text{NaCl-NH}_4\text{Cl-NH}_4\text{HCO}_3\text{-NaHCO}_3\text{-H}_2\text{O}$  system:  
(a)—15 °C—isotherm; (b)—0, 15 and 30 °C—isotherms

system is known, the content of the salts expressed in mole per cent can be found, since the number of moles of all the salts in the system is equal to the number of moles of cations or anions contained (100%). To show the amount of water in the saturated solutions, isohydric lines are drawn on the diagram (Fig. 40), i.e. lines of equal water content. The numbers on the isohydric lines give the number of moles of water per mole total salts of the dry remainder.

In carrying out the carbonation process commercially, it is important that the conditions selected provide maximum yield of the  $\text{NaHCO}_3$ -precipitate with minimal losses of initial reactants,  $\text{NaCl}$

and  $\text{NH}_4\text{HCO}_3$ . The indexes which describe the degree of utilization of the starting materials—the coefficients of sodium utilization,  $U_{\text{Na}^+}$ , and ammonia utilization,  $U_{\text{NH}_4^+}$  can be calculated from the equations:

$$U_{\text{Na}^+} = \frac{[\text{Cl}^-] - [\text{Na}^+]}{[\text{Cl}^-]} \cdot 100$$

(4.2)

and

$$U_{\text{NH}_4^+} = \frac{[\text{NH}_4^+] - [\text{HCO}_3^-]}{[\text{NH}_4^+]} \cdot 100$$

(4.3)

$U_{\text{Na}^+}$  being the degree of conversion of  $\text{NaCl}$  into  $\text{NaHCO}_3$ -precipitate, %;  $U_{\text{NH}_4^+}$  the degree of conversion of  $\text{NH}_4\text{HCO}_3$  into  $\text{NaHCO}_3$ -precipitate, %;  $[\text{Cl}^-]$ ,  $[\text{Na}^+]$ ,  $[\text{NH}_4^+]$ ,  $[\text{HCO}_3^-]$  the concentrations of the ions in the mother liquor following its carbonation (over the  $\text{NaHCO}_3$ -precipitate). Conditions corresponding to maximum  $U_{\text{Na}^+}$  and  $U_{\text{NH}_4^+}$  values can be found from the solubility diagrams.

The figurative points for starting solutions with different ratios of  $\text{NaCl}$  and  $\text{NH}_4\text{HCO}_3$  in them are located on the diagonal lines which connect the corners of the square corresponding to the given salts. At 15 and 30 °C (Fig. 40*b*) these points are mainly located within the sodium-bicarbonate crystallization field. When  $\text{NaHCO}_3$  is precipitated the composition of the solution changes along a  $\text{NaHCO}_3$ -crystallization ray up to the point of its intersection with curve  $1\text{-}P_2$ ,  $P_2\text{-}P_1$  or  $P_1\text{-}IV$  (depending on the initial ratio of  $\text{NaCl}$  to  $\text{NH}_4\text{HCO}_3$ ).

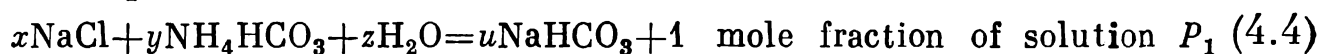
The values of  $U_{\text{Na}^+}$  and  $U_{\text{NH}_4^+}$  depend mainly on the composition of the end solution selected using these curves and on the temperature conditions. Table 6 gives compositions of carbonated solutions calculated using the diagram (Fig. 40*a*) and the corresponding  $U_{\text{Na}^+}$  and  $U_{\text{NH}_4^+}$  values.

TABLE 6

$U_{\text{Na}^+}$  and  $U_{\text{NH}_4^+}$  Values for Equilibrium Composition of Carbonated Solutions at 15 °C

Point on the diagram	Salt concentration of the starting solution, g per 1000 g H <sub>2</sub> O		Ion concentrations of the end solution, g-equivalents per 1000 g H <sub>2</sub> O				$U_{\text{Na}^+}$ , %	$U_{\text{NH}_4^+}$ , %
	NaCl	NH <sub>4</sub> HCO <sub>3</sub>	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>		
$P_2$	479	295	0.18	8.17	4.62	3.73	43.4	95.1
$b$	417	431	0.51	7.13	2.19	5.45	62.2	90.5
$P_1$	397	496	0.92	6.79	1.44	6.27	78.8	85.1
$c$	351	446	0.99	6.00	1.34	5.65	77.7	82.5
$d$	316	412	1.07	5.41	1.27	5.21	76.4	79.5
$e$	234	327	1.30	4.00	1.16	4.14	71.0	68.6

**Example.** To calculate the composition of the starting solution and the utilization coefficients for obtaining a carbonated solution of composition  $P_1$  (with respect to one mole fraction of the solution) the equation for isothermal crystallization is written



From the diagram (Fig. 40a) the composition of solution  $P_1$  is found in moles per mole dry remainder: 0.186  $\text{Na}^+$ , 0.814  $\text{NH}_4^+$ , 0.88  $\text{Cl}^-$ , 0.12  $\text{HCO}_3^-$  and 7.2  $\text{H}_2\text{O}$ . Then, the member equations are written down: for  $\text{Na}^+ - x = u + 0.186$ ; for  $\text{Cl}^- - x = 0.88$ ; for  $\text{NH}_4^+ - y = 0.814$ ; for  $\text{HCO}_3^- - y = u + 0.12$ , and for  $\text{H}_2\text{O} - z = 7.2$ . From these equations we find  $u = x - 0.186 = 0.88 - 0.186 = 0.694$ .

It follows that for obtaining 1 mole fraction of solution  $P_1$  and 0.694 mole of  $\text{NaHCO}_3$  precipitate, 0.88 mole of  $\text{NaCl}$ , 0.814 mole of  $\text{NH}_4\text{HCO}_3$  and 7.2 moles of  $\text{H}_2\text{O}$  must be mixed together. The solution is supersaturated\* at 15 °C since the saturated solution corresponding to the initial point  $a$  (Fig. 40) contains approximately 25 moles of water. Crystallization of  $\text{NaHCO}_3$  will continue from such a solution until the solution composition reaches point  $P_1$ . The ratio between the starting reactants in this case is

$$\frac{\text{NaCl}}{\text{NH}_4\text{HCO}_3} = \frac{0.88}{0.814} = 1.08$$

The utilization indexes for an end solution of composition  $P_1$  are

$$\begin{aligned} U_{\text{Na}^+} &= \frac{100 (\text{Cl}^- - \text{Na}^+)}{\text{Cl}^-} = \frac{\text{NaHCO}_3_{\text{prec}} \cdot 100}{\text{NaCl}} = \\ &= \frac{100 (0.88 - 0.186)}{0.88} = \frac{0.694}{0.88} \cdot 100 = 78.8\% \\ U_{\text{NH}_4^+} &= \frac{100 (\text{NH}_4^+ - \text{HCO}_3^-)}{\text{NH}_4^+} = \frac{\text{NaHCO}_3_{\text{prec}} \cdot 100}{\text{NH}_4\text{HCO}_3} = \\ &= \frac{(0.814 - 0.12) \cdot 100}{0.814} = \frac{0.694 \cdot 100}{0.814} = 85.1\% \end{aligned}$$

From Fig. 40 and Table 6 it follows that  $U_{\text{Na}^+}$  grows with an approach to point  $P_1$ , where it reaches its maximum value, and  $U_{\text{NH}_4^+}$  grows in the direction of point  $P_2$ , where it also reaches a maximum. Theoretically best results are obtained in the vicinity of point  $P_1$  where maximum  $U_{\text{Na}^+}$  values are accompanied by rela-

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\* Actually the brine subjected to carbonation is not supersaturated, since under industrial conditions it is impossible to obtain even full saturation of the initial salt brine. Besides, the drop in the temperature of the suspension (to 20-25 °C) only occurs in the bottom part of the carbonation tower, at the end of  $\text{NaHCO}_3$ -crystallization.

tively large  $U_{\text{NH}_4^+}$  values. Consequently, at 15 °C the maximum theoretical  $\text{NaHCO}_3$  yield (with respect to  $\text{NaCl}$ ), when crysallization ends, comprises only 78.8%.

The equilibrium in the system under consideration changes with the temperature. The table contains values of  $U_{\text{Na}^+}$  and  $U_{\text{NH}_4^+}$  calculated for points  $P_1$  and  $P_2$  (Fig. 40) at various temperatures.

Points	Tempera- ture, °C	Utilization coefficient, %	
		$U_{\text{Na}^+}$	$U_{\text{NH}_4^+}$
$P_1$	0	73.6	88.0
$P_1$	15	78.8	85.1
$P_1$	30	83.5	84.2
$P_2$	0	35.6	95.6
$P_2$	15	43.4	95.1
$P_2$	30	50.7	94.2

It follows that when the temperature is increased,  $U_{\text{Na}^+}$  grows, whereas there is practically no change in  $U_{\text{NH}_4^+}$ . The maximum theoretical  $\text{NaHCO}_3$  yield is achieved at 32 °C (point  $P_1$ ) and is equal to 84%. The composition of  $P_1$  at 32 °C corresponds to point  $f$  for the starting solution (Fig. 40), which lies at the intersection of the diagonals of the square and corresponds to equimolecular amounts of the starting reactants  $\text{NaCl}$  and  $\text{NH}_4\text{HCO}_3$ .

Commercially, the  $\text{NaHCO}_3$  yield always lies below the theoretical value, primarily because compositions of carbonated solutions corresponding to point  $P_1$  (Table 6, Fig. 40*b*) cannot be realized under industrial-process conditions.

At soda plants solutions not saturated with respect to  $\text{NaCl}$  are subjected to carbonation and the carbonated solutions do not contain more than 270 g/l  $\text{NaCl}$  and approximately 90 g/l  $\text{NH}_3$  (total ammonia content). Therefore, the practical  $\text{NaHCO}_3$  yield (with respect to  $\text{NaCl}$ ) usually comprises 65-75%, depending on the temperature, the  $\text{NaCl}$ -content of the brine, the degree of its saturation with ammonia and carbon dioxide, and on other factors.  $U_{\text{Na}^+}$  can be raised by increasing the content of  $\text{NaCl}$  and  $\text{NH}_3$  in the ammoniated brine, by increasing the concentration of  $\text{CO}_2$  in the gas used for carbonation, by lowering the temperature of the final part of the carbonation process, etc.

The temperature conditions in the carbonation tower are especially important. In the central part of the tower, where the  $\text{NaHCO}_3$  crystals are formed, cooling is not necessary, since a rise in the temperature to 40-50 °C (at the expense of exothermic reactions) promotes formation of large crystals, which leads to good filtering. At the bottom of the tower, where the final stage of crystallization

takes place, the temperature should be lowered to decrease the solubility of  $\text{NaHCO}_3$  (see Fig. 40b) and increase its yield by additional precipitation of crystals from the cooled solution.

The solubility diagrams of the  $\text{NaCl-NH}_4\text{HCO}_3\text{-H}_2\text{O}$  system show that it is not possible theoretically to attain complete conversion of common salt into sodium-bicarbonate precipitate. This is one of the basic drawbacks of the ammonia-soda manufacturing process.

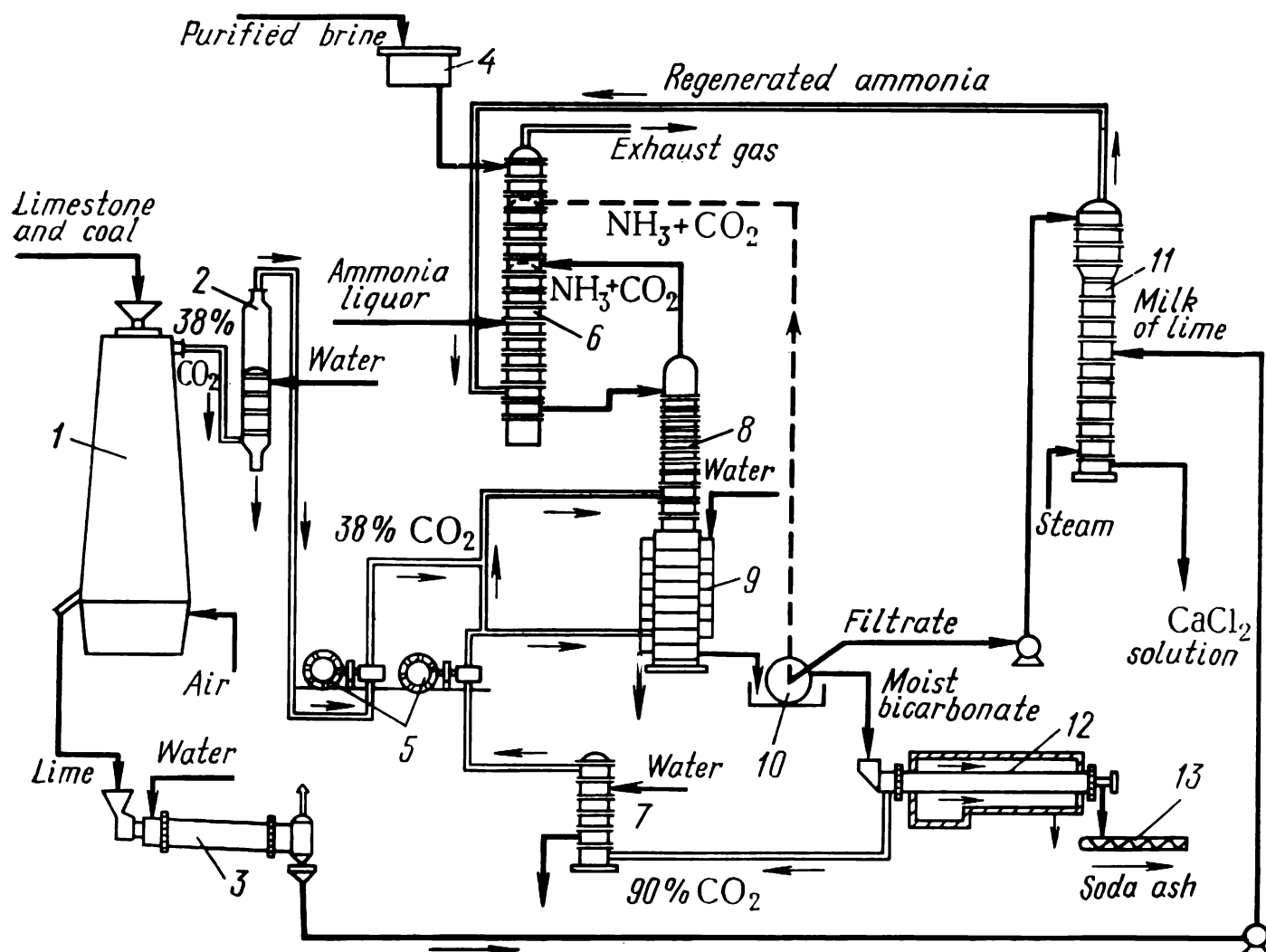
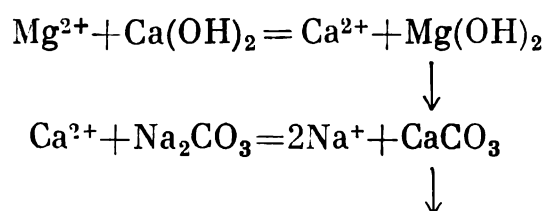


Fig. 41. Flow diagram of soda manufacturing by the ammonia method:

1—limestone calcining shaft furnace; 2, 7—kiln-gas scrubbers; 3—lime slaker; 4—brine head-tank; 5—compressor; 6—tray-type absorption tower; 8—tray-type carbonization (precipitation) tower; 9—lower, cooled, part of tower; 10—revolving drum vacuum-filter; 11—tray-type distillation tower; 12—sodium bicarbonate calcination kiln; 13—conveyor

A flow-diagram of a soda manufacturing process, considerably simplified, is given in Fig. 41. Soda manufacturing begins with preparation and purification of the common-salt solution (not shown in the diagram). The brine obtained by underground leaching of salt-deposit layers, or a naturally occurring brine, has additional amounts of rock salt dissolved in it in saturators and its concentration is brought up to 305-310 g  $\text{NaCl/l}$ .

Before it is used in the ammonia-soda process, salts of calcium and magnesium must be removed from the brine, since otherwise these salts will precipitate during ammoniation and carbonation of the brine, clog the apparatus and disrupt normal operation. The  $\text{Ca}^{2+}$ - and  $\text{Mg}^{2+}$ -cations are removed by precipitating the impurities with carefully measured amounts of precipitating reagents—a suspension of soda in purified brine and milk of lime (the soda-lime method). Precipitation of the impurities takes place, for example, by the reactions:



The magnesium hydroxide and calcium carbonate precipitates are separated in continuous-action thickeners. The purified and clarified brine from head tanks (Fig. 41) located on the top floor of the multistorey soda-ash manufacturing plant flows by gravity into tray-type columns (absorbers), where the brine is saturated with ammonia and, to a certain extent, with carbon dioxide. For this purpose regenerated ammonia from the ammonia stills and also the spent gases from the various apparatus of the plant (the carbonation towers, absorbers, filters) containing a remainder of ammonia and carbon dioxide are used. Absorption is carried out in several consecutive absorbers. After each stage the heat of the reaction is removed in external, atmospheric, drip coolers (not shown on the diagram). To compensate for ammonia lost, ammonia liquor is introduced into the absorbers (approximately 2.5 kg  $\text{NH}_3$  per ton of soda ash produced).

The ammoniated brine moves from the absorption section to the carbonation section and is distributed to the carbonation towers. These are bubble-tray columns with coolers, through which cold water circulates, in the lower part. Concentrated carbon dioxide gas from the soda-ash calcination kiln and weak furnace gas from the lime kilns are fed by compressors to the bottom and central parts of the tower.

The bicarbonate suspension from the towers flows by gravity to the filtration section. In drum-type, rotary, vacuum filters moist bicarbonate is separated from the mother liquor (filtrate) and is transferred by conveyers to calcining furnaces (driers). These are rotary drum furnaces heated from the outside using combustion gases produced by burning natural gas, or liquid or pulverized solid fuels. The combustion gases flow through the annular space between the fire-brick lining of the furnace and the outer walls of the calciner cocurrent to the bicarbonate being calcinated. The temperature



inside the calciner is 140-170 °C\*. The moist bicarbonate is fed into the loading part of the calciner by a special feeding device, and the soda-ash product is removed from the discharge end by worm conveyers and transferred to the packing section on a conveyor belt.

The gases from the calcining process, which contain water vapour and about 90% CO<sub>2</sub> (with respect to the dry gas), are removed from the loading end of the calciners and, after being cooled and washed with water in scrubbers, they are fed to the carbonation towers by a compressor.

The filtrate goes from the filters to the section for ammonia regeneration. This section contains heat exchangers in which the liquid is heated by gases leaving the stills, where the combined ammonia (NH<sub>4</sub>Cl) is decomposed. The filtrate is fed to the stills in a mixture with milk of lime, obtained by slaking lime. Steam, the heating agent, is introduced at the bottom of the still.

The calcium-chloride solution produced is removed from the bottom of the ammonia still to sludge basins located outside the plant territory. Up to 9 cu m of the CaCl<sub>2</sub> solution is discharged by the plant per ton of soda ash produced. The still gases, containing the ammonia, are cooled in a number of heat exchangers (not shown in the diagram) and then fed to the absorbers. The lime, from which the milk of lime is made in the slaker, and a gas containing 35-40% CO<sub>2</sub> are produced in lime kilns. Dust is removed from the lime-kiln gas, which is then cooled in a scrubber and fed to the carbonation towers by a compressor.

Most of the processes involved in manufacturing soda ash are based on mass and heat transfer during direct contact between gases and liquids. Therefore, the basic apparatus employed in soda plants is principally of the same type—in the form of tray columns built up of cast iron sections or drums. The drums at the bottom (the base) and the top of the tower are either empty or they may contain gas-distribution or spray-separation devices; the drums in the central part of the tower contain bubble-cap trays. Absorbers, heat exchangers and scrubbers usually contain trays with a number of bubble caps on them to increase the area of interface contact for heat- and mass transfer. The apparatus through which liquids containing suspended particles flow or where precipitates are formed—carbonation towers and ammonia stills—contain trays with a single bubble cap. In multitray bubbler towers of the soda manufacturing process the liquid on each tray is roughly completely mixed. However, since there are a large number of trays plug flow is approached

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\* At the present time soda manufacturing plants are changing over to the more efficient method of steam calcination in drum reactors or reactors with a fluidized bed of the moist bicarbonate.

and in reactor calculations relationships for ideal plug flow can be employed.

Approximate consumption factors per ton soda ash produced (95%  $\text{Na}_2\text{CO}_3$ ) are given in the following table.

Purified brine (310 g $\text{NaCl/l}$ ), $\text{m}^3$	5.0
Ammonia liquor (25% $\text{NH}_3$ ), kg	10.0
Limestone (100% $\text{CaCO}_3$ ), kg	1100
Steam for the process, J	$5.24 \cdot 10^6$
Electric power, kWh	40
Coke*, kg	90
Fuel oil*, natural gas*, kg	120
Water, $\text{m}^3$	75

*The most important ways of improving soda manufacturing are:* increasing unit production-capacity, raising raw-material utilization indexes, lowering consumption coefficients, and also achieving maximum possible utilization of the process off-products. The principal features of recent developments in the USSR are larger plants, improved technological processes, introduction of improved apparatus designs, total mechanization of all processes where much labour is involved—packaging, storing and moving the soda—automatic control of all stages of the process. There are outstanding achievements in the field of integral automation of the ammonia-soda manufacturing process and in employing computers in the control system.

The most important negative feature of the ammonia process for making soda, which limits its growth, is the generation of a tremendous volume of effluent liquid, solutions of calcium chloride, which pollute the aquasphere. Feasible methods for utilizing these waste products—the manufacture of calcium chloride from the effluent distiller liquid or the manufacture of nitrogenous fertilizers ( $\text{NH}_4\text{Cl}$ ) from filtrates—do not provide utilization of more than 15% of the total amount of chloride waste. Because of this, all over the world it has become imperative to find new, less costly, less ecologically harmful methods for making soda, which provide complete utilization of the raw materials with no waste discharge.

In the USSR the best perspectives belong to the manufacture of soda from naturally-occurring nepheline raw materials, which contain carbonate alkalies, by their integral processing to yield aluminium, Portland cement, soda and potash. The process is featured by lower cost of the products, in particular, of soda ash, than at specialized plants, and also by complete absence of waste products and harmful effluents. In the near future in the USSR more than 25% of all the soda ash will be made in this way and in all probability the manufacture of soda from nephelines, of which there are very large deposits, will to a very large degree replace the ammonia process.

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\* In terms of an arbitrary fuel with a calorific value of  $29.3 \cdot 10^3$  kJ/kg.

### 1. Industrial Silicate Products and Their Applications

The technology of silicate processes is concerned with the production of minerals or their mixtures, wares made from them, and also of different kinds of glass and glass ware. The materials and wares manufactured in the silicate industry possess diverse and valuable properties. The properties typical of most silicates result from the specific structure of their molecules, the basic structural element being the tetrahedric group  $\text{SiO}_4^{4-}$ . A characteristic feature of this structure is the high strength of the bond between the  $\text{Si}^{4+}$  and  $\text{O}^{2-}$  ions, as a result of which most silicates are extremely hard and have a high melting point. Other properties common to most silicates are chemical stability, resistance to high temperatures, and also comparatively low cost, due to the availability of the raw materials.

*The raw materials* for the silicate industry are very widespread in nature, where they are found in the form of deposits of such common minerals as clays, marls\*, limestone, chalk, dolomite, quartz sand, tuff, tripoli, quartzite, feldspars, nepheline, etc. Besides naturally occurring raw materials, various synthetic and artificial raw materials are used in manufacturing silicates—soda ash, borax, sodium sulphate, oxides and other compounds of various metals, etc. Waste products of ferrous and non-ferrous metallurgy and of a number of chemical industries—blast-furnace slag, shale cinder, nepheline sludge of alumina-manufacturing processes, etc.—can be utilized as raw materials for the silicate industry. At present, silicate technology covers the production of many minerals and products which do not contain silicon dioxide and its compounds, for instance, the manufacture of high-refractory oxides and wares from them—cermets, magnesia-, chrome-magnesia- and graphite-refractories, air-binding materials (gypsum, lime). Production of these materials and products is nominally classed as belonging to silicate technology due to the use of manufacturing methods similar to those employed in making true silicates.

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\* Marls are deposited minerals, intermediate between limestone and dolomites, and clays, which contain 50-80%  $\text{CaCO}_3$  and  $\text{MgCO}_3$  and 20-50% clay-sand material.

The silicate industry produces extremely important products, and the variety of the different products is tremendous. The silicate industry has several independent branches, of which the most important are the manufacture of ceramics and refractories, cements and plasters, glass and pyrocerams.

*Ceramics* is the name given to ware made from ceramic bodies (mixtures with various amounts of moisture in them which, as a rule, contain clay) by forming or casting, followed by drying and firing to the sintering point. According to their main fields of use ceramic materials and ware can be divided into the following basic groups:

1. Structural ceramics—articles used mainly in constructing buildings and various other structures. Building brick—common brick or hollow tile, brick blocks, roof tile, drain tiles, rock goods (clinker brick, ceramic slabs for floors, sewer pipe, etc.) belong to this group.

2. Facing materials—articles used for internal and external facing of buildings and structures—facing bricks and slabs and oven tiles.

3. Refractories—materials which retain their mechanical properties at high temperatures (above 1000 °C) and which are used in making various parts of industrial furnaces, ovens and apparatus for operation at high temperatures.

4. Fine ceramics—a group which includes wares, mainly porcelain and glazed pottery, used in various fields—domestically (dishes, wash basins, sinks, decorative articles), in the electrical industry (electrotechnical porcelain), in the laboratory (chemical ware and apparatus), etc.

5. Special types of ceramics—a group of articles with specific properties utilized in the radio industry, aviation, instrument manufacture, etc.†

Commercially ceramics are classed as rough wares, which include building materials and refractories, made from coarse-grained ceramic dough and which have a porous biscuit of a non-uniform structure, and fine wares, which include sintered or fine-pore items with a uniform structure of the biscuit—porcelain, glazed pottery and special ceramics.

The raw materials for making ceramics can be divided into three basic groups: (a) plastic materials—clays, (b) non-plastic or leaning admixtures—silica (quartz, sand), crushed chamotte, etc., (c) mineralizers and fluxes, i.e. substances whose addition promotes formation of a liquid phase—feldspar  $[(K, Na)_2O \cdot Al_2O_3 \cdot 6SiO_2]$ , carbonates ( $CaCO_3$ ,  $MgCO_3$ ), etc.

*Cements* is the name given to powdered minerals which when mixed with water form a plastic body that can easily be shaped and that hardens gradually to yield a strong, stone-like body. Depending

on their uses and properties, cements are divided into three main groups: air-hardening cements, which can only harden and retain their strength in air, hydraulic cements, which can also harden and retain their strength in water, and acid-resistant cements which after hardening withstand the action of mineral acids.

Air-hardening cements include air-hardening lime, gypsum- and magnesium cements. These materials are used in making building and plaster mixes (lime), structural and decorative articles (plaster of Paris and magnesia cements).

Hydraulic cements are much more important than air-hardening cements; they are used in making prefabricated reinforced-concrete and concrete structural parts and concrete parts of buildings, underground and hydraulic-engineering structures. The hydraulic cements are hydraulic lime, roman cement, Portland cement and cements with various admixtures (trass cement, slag Portland cement, alumina cements, etc.). Cement is the product of the silicates industry which is manufactured on the largest scale and it is extensively used in building homes, industrial buildings and other structures.

In building practice cements are used in structural pastes of several types: slurries, i.e. mixtures of cement with water; building mortars, mixtures of cement with water and a fine filler (sand); and concretes, mixtures of cement, water, fine and coarse fillers (sand, gravel, crushed rock). The hardened mixture is called concrete and when reinforced with steel, is known as reinforced concrete.

The raw materials used in making cements are naturally occurring materials and in part industrial waste products. The naturally occurring materials include gypsum rock (gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , anhydrite,  $\text{CaSO}_4$ ), limestone rock (limestone, chalk, dolomite), clays—clays and marls, silica sand, bauxites. The industrial waste materials utilized in making cements include metallurgical slag, the nepheline sludge of the alumina-manufacturing industry, sludge of the sodium hydroxide process which contains  $\text{CaCO}_3$ , pyrite cinder, etc.

*Glass* is an amorphous isotropic material created by supercooling molten non-metallic oxides and compounds which do not contain oxygen. Properties common to all types of glass are their valuable optical properties—transparency, uniformity of the optical indexes of large lumps, stability of the optical indexes and the possibility of making a glass with the needed optical characteristics by varying the chemical composition. Other properties also common to glasses are high chemical resistance to the effects of acids and salts solutions, hardness and low heat conductivity. Negative features of glass, which limit its use as a structural material, are friability and poor thermal resistance resulting from the low heat conductivity.

Glasses are classified according to their uses and chemical composition. Approximate compositions and a list of sorts of glass used

in manufacturing consumer goods and industrial items are given in Table 7.

TABLE 7

**Approximate Compositions of Some Glasses Used in Consumer Goods and in Industry**

Kind of glass	Components of glass, % by weight							
	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	PbO	B <sub>2</sub> O <sub>3</sub>
Window glass *	70-73	1.5-2	8-10	3-4	14-15	—	—	—
White bottle *	69-72	3-4	9-10	2-4	15-16	—	—	—
High-grade dinner ware	73-75	—	6-10	0-3	15-16	0-3	—	0-1
Crystal	55-77	—	—	—	—	10-13	30-35	—
Chemical resistant	68-70	3-5	6-8	1-2	8-10	5-6	—	2-3
Optical ** (flint glasses)	47-65	—	—	—	—	6	45	—
Lighting *** (dispersing)	69-73	4-6	4-5	—	11-16	2-6	—	—
Electrovacuum ****	69-70	—	5-6	3-4	12-13	4	—	—
Glass fibre	48-56	10-18	5-16	0-8	0.5-2	—	—	6-13

*Note:* Some of the types of glass also contain other components: \* Up to 0.5% Fe<sub>2</sub>O<sub>3</sub>; \*\* 0.25% As<sub>2</sub>O<sub>3</sub>; \*\*\* up to 6% ZnO; 4-9% F; \*\*\*\* 5% BaO.

The raw materials from which glass is made must contain glass-forming oxides, i.e. acid, alkaline, alkaline-earth and other oxides which form the glass body and which yield a glass with the required properties. Such materials are quartz sand, boric acid and borax, soda ash, sodium sulphate or potash (K<sub>2</sub>CO<sub>3</sub>), limestone or chalk, magnesite, barite (BaSO<sub>4</sub>) or witherite (BaCO<sub>3</sub>), kaolin (Al<sub>2</sub>O<sub>3</sub> × 2SiO<sub>2</sub>·2H<sub>2</sub>O), minium (Pb<sub>3</sub>O<sub>4</sub>) or litharge (PbO), zinc carbonate, nepheline [(Na, K)<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>], feldspars (alumosilicates of sodium, potassium, calcium) and also crushed glass and waste products of other processes, for example blast-furnace slag.

In recent years scientists and engineers in the silicate industry are devoting their efforts toward creating structural materials which meet the requirements of the radioelectronics, aviation, semiconductor, nuclear, rockets technologies. The new materials should have a combination of features such as high mechanical strength, especially high refractory properties, chemical and thermal stability as well as specific electrical or radioelectronic, etc. properties. Materials with high resistance to corrosion, or refractory properties, and which are also readily available for wide-scale use are very important in chemical engineering. Silica ceramics and pyrocerams belong to this category. Quartz ceramics is made from quartz sand

or rock crystal (for transparent items) by pressforming or casting and firing to the sintering point. For making heat insulating materials (foamed quartz ceramics) in the forming process foaming agents are added. Quartz ceramics possesses the properties of high chemical and thermal stability, low temperature expansion, excellent electrophysical parameters and low heat conductivity resulting from its porosity. It is used on a broad scale in the chemical industry, in making electric insulation materials, in rocketry.

*Pyrocerams*—materials made of uniformly crystallized glass—lie between glasses and ceramics. Pyrocerams are stronger than glass, harder than high-carbon steel, have high chemical and thermal resistance, excellent dielectric properties and low temperature expansion. To make pyrocerams, in the glass melt centres of crystallization are formed on which the crystals of the principal phase, which determines the properties of the material, grow. By varying the properties of the starting-material glass pyrocerams with given desired properties can be obtained.

## 2. Typical Silicate-Technology Operations

There is much in common in the technological operations used for producing the diverse silicate materials, since most silicate-technology processes have common physicochemical principles. The technological schemas employed in manufacturing various silicates (ceramic items, refractories, cements) are, as a rule, made up of typical unit processes and operations. Common to all of them are the purely mechanical operations of crushing, grinding and mixing the solid materials in preparing the charge from the raw materials, and also the physicochemical processes, which are accomplished by subjecting a charge to high temperatures to form a given mineral or a mixture of minerals.

The preparation of the mixture of raw materials in manufacturing a silicate must be such as to provide high intensity of the firing-, sintering- or melting-high-temperature processes which follow and serve to form a material or article with the desired properties and composition. The solid raw materials are finely ground, accurately measured and introduced into the mixture; the charge is thoroughly mixed, moistened, and the ware is formed by bricketing or molding and the formed ware is dried to guard against changes in composition or the shape of the ware during firing (in the manufacture of ceramics).

The basic operation in making any silicate is high-temperature processing of the charge; it results in synthesis of minerals and formation of glass (or of a glass phase in a sintered material). Therefore, for silicate technology, the knowledge of the physicochemistry of the processes which take place when a silicate charge is heated

is of primary importance. The acid oxides most often used in silicate technology are  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{B}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$  and the basic oxides are  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{MgO}$  and others. When a silicate charge containing these oxides (in the form of their carbonates, aluminosilicates, or hydrates) is heated the following elementary processes take place consecutively: loss of physical and hydrate-form moisture, calcination (loss of constitutional water and  $\text{CO}_2$ ), weakening of the crystal lattice and its rearrangement by polymorphic conversions, diffusion of the reagents, formation of solid solutions, sintering, melting, crystallization from the molten mass, sublimation and, finally, in many of the processes, the formation of eutectics and new chemical compounds.

**Reactions in the solid phase.** One of the stages of formation of a mineral when a charge is heated consists of processes in the solid phase.

The processes involved in making many ceramic products, and also cements, to a certain degree occur by reactions between solid substances at temperatures lying below those at which significant amounts of molten materials are formed. Heating a charge in the solid phase results in changes in the crystal lattice, formation of solid solutions, diffusion and chemical reactions. If there are no liquid- or gas-phase materials present, diffusion of reactants and chemical reactions proceed at extremely low rates. Actually, under industrial conditions reactions in mixtures of crystalline substances take place with participation of a liquid phase and a gas phase, formed in small amounts by dissociation, sublimation and fusion of the crystals. Fusion is often caused by admixtures or impurities in the solid mixture which are fluxing substances (mineralizers), i.e. which form low-melting-point eutectics with its components.

If the mixture of solid substances is heated still further, visible amounts of liquid appear, and as a result the rate of diffusion and chemical reactions increases. Final formation of minerals of the desired composition ends in sintering or melting of the mixture being heated, and this is followed by cooling.

*Sintering* is a highly important process resulting from heating a mixture of solid substances. In silicate technology it is the final stage in firing ceramics, refractories and cement; sintering results in the formation of the final, high-strength ceramic biscuit, and of the minerals of cement clinker.

A distinction is made between sintering in the solid phase and sintering with a liquid phase participating. Solid-phase sintering consists in filling the spaces inside the grains (the pores) and the interstitial spaces between the grains. This occurs as a result of increased mobility of the atoms in the crystal lattice at high temperatures. Simultaneously, the grains recrystallize, i.e. some of the crystals grow in size at the expense of others. The rate of solid-phase



sintering depends on grain size and on the presence of defects in the crystal lattice and it grows with a decrease in the size and an increase in the number of defects.

Most often in industrial processes sintering occurs with a liquid-phase participating; this is a diffusion process and its course depends on the amount of the molten mass which fills the space between the grains, and its properties. The sintering rate increases with decreased viscosity of the molten mass and an increase in its wetting ability.

Sintering is accompanied by formation of new chemical compounds resulting from the appearance of a liquid phase and reactions between components of the molten or sintered mass.

When sintered materials are cooled a crystal lattice either of the type which existed or of a new one may be formed. Under certain conditions cooling a molten mass yields an amorphous substance—a glass, and not a crystalline one. The presence of a glass phase is a typical feature of many end-product silicate materials or wares.

*Phase diagrams and heating curves* are used for investigating the changes in the properties of complex silicate systems during heating and cooling; they are plotted from experimental data and they show the most important property of the system—the changes in the melting point, or crystallization point, with composition.

Phase diagrams give the clearest picture of interaction between components of a silicate system and compounds formed, between solid and liquid phases, and of any other processes which take place. Using a phase diagram, one can determine the chemical composition of the various phases, the temperatures at which melting or crystallization begins and ends, and the change in the ratio of the liquid and solid phases. In industrial practice phase diagrams and heating curves are used to determine the composition of the charge to be subjected to firing, sintering or melting; to determine the desirable temperature conditions in the various zones of the furnace, the period during which it must be kept at each temperature, etc.

*Silica* can exist in various forms—in a crystalline form, as  $\alpha$ - and  $\beta$ -quartz;  $\alpha$ -,  $\beta$ - and  $\gamma$ -tridymite;  $\alpha$ - and  $\beta$ -cristobalite\* or in a non-crystalline form—as quartz glass. All of these forms have commercial importance and there are a number of modifications of each of them, stable in certain temperature limits. When the temperature changes a polymorphic conversion of one form, or modification, of the silicon dioxide into another occurs, and this is the basis of high-temperature processing of the silicate charge and determines the properties of the ware produced.

These conversions can be traced on the silicon dioxide phase diagram (Fig. 42), which shows how the stability of the silicon

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\* The form which is stable at the highest temperature is denoted by  $\alpha$ , the next in order by  $\beta$ , etc.

dioxide modifications changes with the temperature. The measure of the stability is the vapour pressure, which at a given temperature has a minimum value for the most stable modification. Each curve of the diagram corresponds to one of the four silicon dioxide forms. The dashed lines correspond to an unstable state of the given modification and the solid lines to a stable state.

It is evident from the diagram (Fig. 42) that the most common form of silicon dioxide, quartz, is stable up to 870 °C, where the

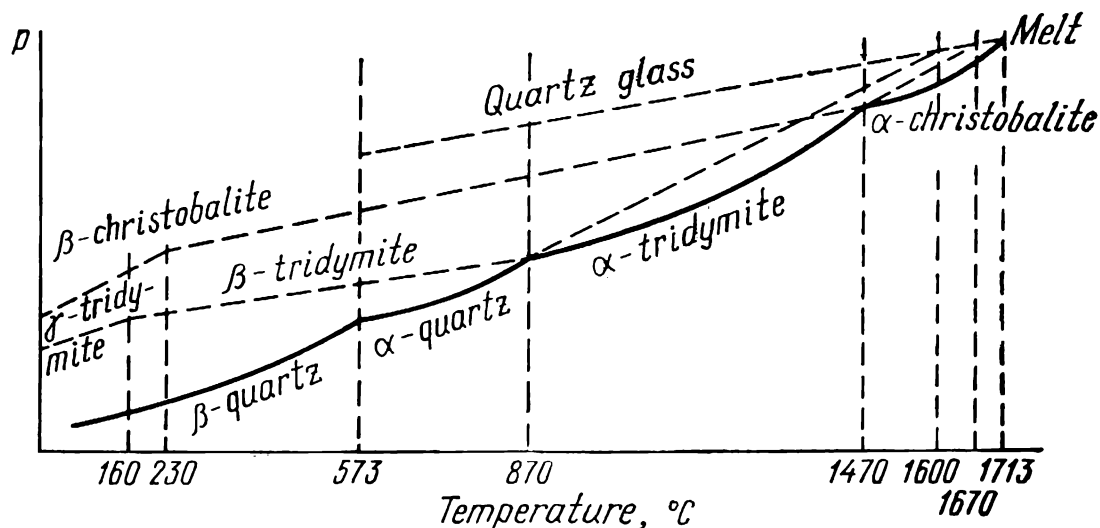


Fig. 42. Phase diagram for the SiO<sub>2</sub>-system

quartz curve intersects the tridymite curve. At 573 °C β-quartz transforms into α-quartz, which is not stable from 870 °C up to 1600 °C, i.e. up to the melting point. Transformation of α-quartz directly into tridymite without the use of special admixtures practically does not occur. Under equilibrium conditions α-quartz undergoes a number of complex conversions and at 1200-1470 °C it is partially changed into the christobalite modification (via the metastable phase of α-christobalite which is also called metachristobalite).

The remaining forms of silica are unstable at temperatures below 870 °C. The most important commercial modification—α-tridymite (melting point 1670 °C) is stable in the temperature interval from 870 °C to 1470 °C, above which it changes into α-christobalite, which has the highest melting point (1713 °C). Christobalite is stable only at temperatures above 1470 °C in the α-christobalite modification.

The metastable modification, β-christobalite, can exist under ordinary conditions and it is found in nature, but when heated above 240 °C it quickly transforms into the α-modification. This transformation results in a significant increase in volume. The various forms of silica melt when heated to 1700-1800 °C. If the molten mass is supercooled to below the melting point of christobalite the least stable form of silica with the highest vapour pressure—quartz (silica) glass—is formed.

Under equilibrium conditions the interconversions of quartz, tridymite and cristobalite occur at a very low rate, and, industrially, for such conversions to take place mineralizer admixtures, which form fusible eutectics with  $\text{SiO}_2$ , are necessary. The transformations from one silica modification to another during thermal treatment result in changes in properties, in particular, in a change in density.

The change in volume which occurs during transformation of one  $\text{SiO}_2$ -modification to another is of extreme practical importance in the processes of making materials and wares containing large amounts of silicon dioxide (Dinas and aluminosilicate refractories, quartz glass); considerable changes in volume during thermal treatment may cause cracking and spoilage. From this point of view, the best form is tridymite, for which expansion during transformation from one modification to another is minimum as compared with quartz and cristobalite.

For obtaining tridymite in Dinas and chamotte refractory ware in the production process admixtures are introduced, i.e. mineralizers, which form a liquid phase with the quartz and accelerate the slow process of transformation of quartz to the stable, tridymite modification. The presence of a liquid phase in the material also reduces the destructive effect of expansion and compression of the crystals. The changeover from quartz to tridymite in the presence of mineralizers ( $\text{CaO}$ ,  $\text{FeO}$ ,  $\text{MgO}$ ) occurs in the temperature interval of 1200-1470 °C. To facilitate this, during firing of Dinas articles the temperature is raised slowly, especially in the interval from 1350 to 1450 °C (the final firing temperature), where the rate of heating is not allowed to exceed 3-5 °C per hour. The tridymite is mainly formed during lengthy heating within this temperature interval, whereas rapid temperature rise promotes formation of cristobalite, which occurs more readily.

*Alumina* has several crystalline modifications, of which two are stable:  $\alpha\text{-Al}_2\text{O}_3$ , or corundum, which possesses very great hardness and chemical stability and  $\gamma\text{-Al}_2\text{O}_3$ , which is hygroscopic and soluble in acids and bases. When heated to above 950 °C  $\gamma\text{-Al}_2\text{O}_3$  changes into  $\alpha\text{-Al}_2\text{O}_3$ . Alumina is included in the charge for making ceramic articles, refractories, cements, mainly in the form of aluminosilicates contained in clays or marls.

The  $\text{Al}_2\text{O}_3\text{-SiO}_2$  system, whose phase diagram is given in Fig. 43, is of great importance in the technology of ceramics and refractories.

It is evident from the diagram that in this system one chemical compound, mullite,  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ , and two eutectics can form in the solid phase. *Mullite* has excellent refractory properties (melting point 1910 °C) and is chemically stable to the action of acids and molten slag. The  $\text{Al}_2\text{O}_3\text{-SiO}_2$  diagram is especially important in the technology of aluminosilicate refractories. It shows the change in the basic composition and properties during manufacturing semi-

acid refractories (70-90%  $\text{SiO}_2$  and 10-30%  $\text{Al}_2\text{O}_3$ ), chamotte (53-65%  $\text{SiO}_2$  and 30-45%  $\text{Al}_2\text{O}_3$ ) and high-alumina-content (45-100%  $\text{Al}_2\text{O}_3$ ) refractories, and also aids in the selection of the initial materials (refractory clays and kaolins) and admixtures.

The diagram shows that mullite,  $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  (71.8%  $\text{Al}_2\text{O}_3$  and 28.2%  $\text{SiO}_2$ ), which is stable at high temperatures (above

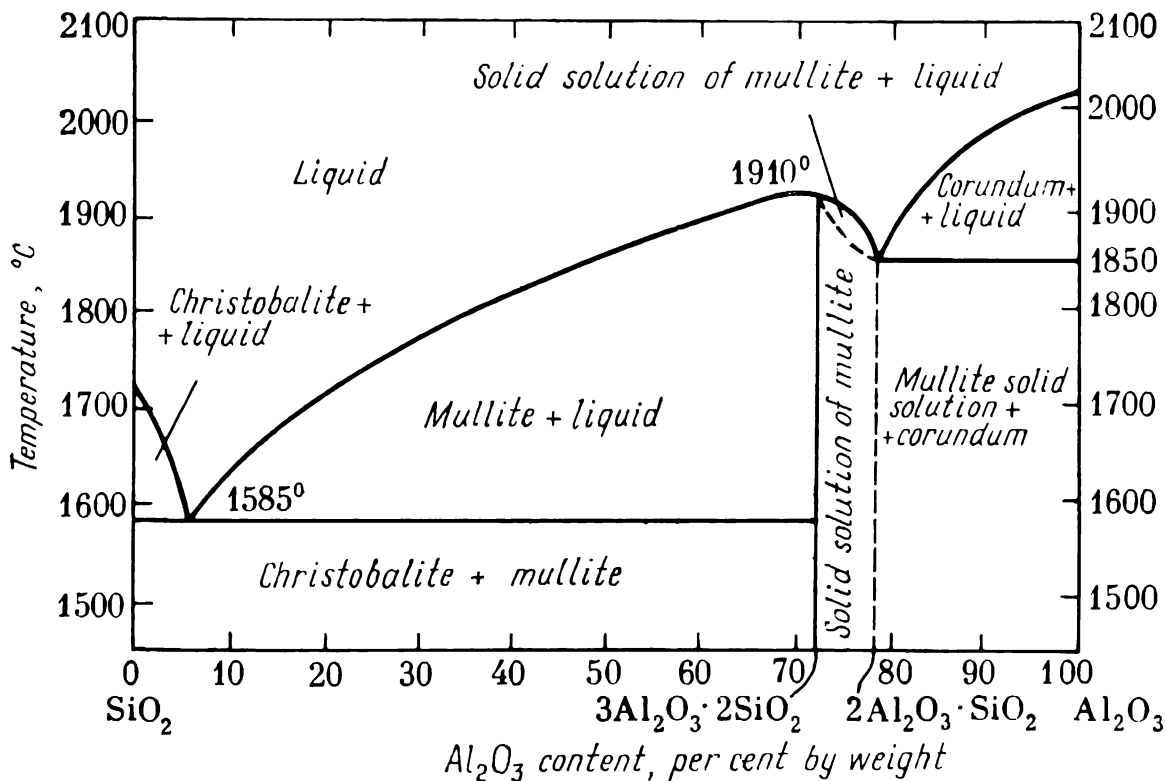


Fig. 43. Phase diagram for  $\text{Al}_2\text{O}_3$ - $\text{SiO}_2$  system

1585 °C), forms the basis of the solid phase of aluminosilicate refractories. The presence of mullite gives the articles their refractory properties and high chemical resistance.

The formation of mullite takes place during firing of the ware, beginning with a temperature of 1000 °C. The maximum amount of mullite is formed at 1600 °C, or, if there are admixtures (fluxes) present in the initial clays, at 1400 °C. Actually, the yield of mullite is always less than the equilibrium amount and depends mainly on the composition of the initial materials and on how close the  $\text{Al}_2\text{O}_3$  content of the latter is to the stoichiometric value (71.8%). According to the diagram, at temperatures above 1585 °C, besides mullite, there is a liquid phase (molten mass) present in the material and this results in sintering of refractory materials (and other ceramic ware), a vitreous phase being formed in the ware. The principal components of the liquid phase are silica and the fluxing admixtures. The amount of the molten mass at equilibrium can be found using the diagram, by the lever rule, from the ratio of solid and liquid phases. Actually in the presence of admixture fluxes ( $\text{Fe}_2\text{O}_3$ ,  $\text{CaO}$ ,

etc.) which are part of the initial clay material, molten matter is formed and ceramic ware sinter at lower temperatures. These factors govern the temperature regime for firing refractories and other ceramics. For example the final firing temperature for chamotte ware is 1350-1400 °C, whereas at equilibrium (Fig. 43) the temperature would have to be raised to above 1600 °C for mullite to form and molten material to appear. For formation of tridymite

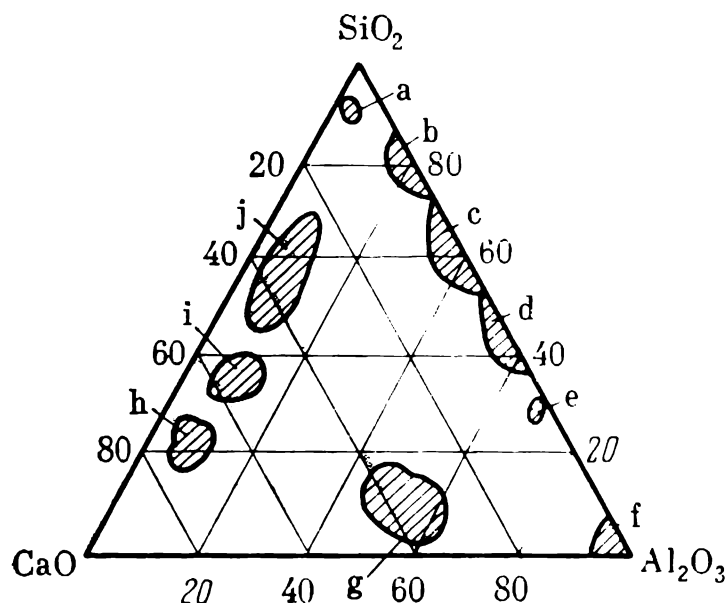


Fig. 44. Composition of the most important silicate materials based on CaO,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ :

*a*—Dinas; *b*—semi-acid refractories; *c*—chamotte; *d*—high-alumina refractories; *e*—mullite; *f*—corundum; *g*—aluminous cements; *h*—Portland cement; *i*—basic slags; *j*—acid metallurgical slags

in the chamotte the temperature during firing must be raised even slower, and the final firing temperature must be maintained for a longer time, than in making Dinas.

Carbonates of calcium, magnesium or sodium are almost always a part of the charge used in making a silicate. When heated the carbonates decompose to form the corresponding oxides ( $\text{CaO}$ ,  $\text{MgO}$ ,  $\text{Na}_2\text{O}$ ). These basic oxides react at high temperatures and form chemical compounds with acidic and amphoteric components of the silicate charge—silica, alumina and iron oxide.

The system  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  is of especial importance for silicate technology. Various compounds which can form in this system comprise highly important products of the silicate industry (Fig. 44). The phase diagram of the  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  system given in Fig. 45 shows the composition of the chemical compounds and eutectics which form under different conditions in this complex system.

In glass technology the processes of synthesis of silicates which take place in the molten mass during the glass-cooking operation are highly important. Knowledge about these processes was obtained by thermal analysis of the reactions between the components of the

silicate charge ( $\text{Na}_2\text{CO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{SiO}_2$ ) during heating. The heating (cooling) curves for the mixture are given either in coordinates of temperatures vs time or difference of temperatures of a standard and the sample vs temperature. In the latter case (the differential method of thermal analysis) the sample and a standard substance, which does not undergo phase transformations, are heated (cooled) in identical conditions. An automatic

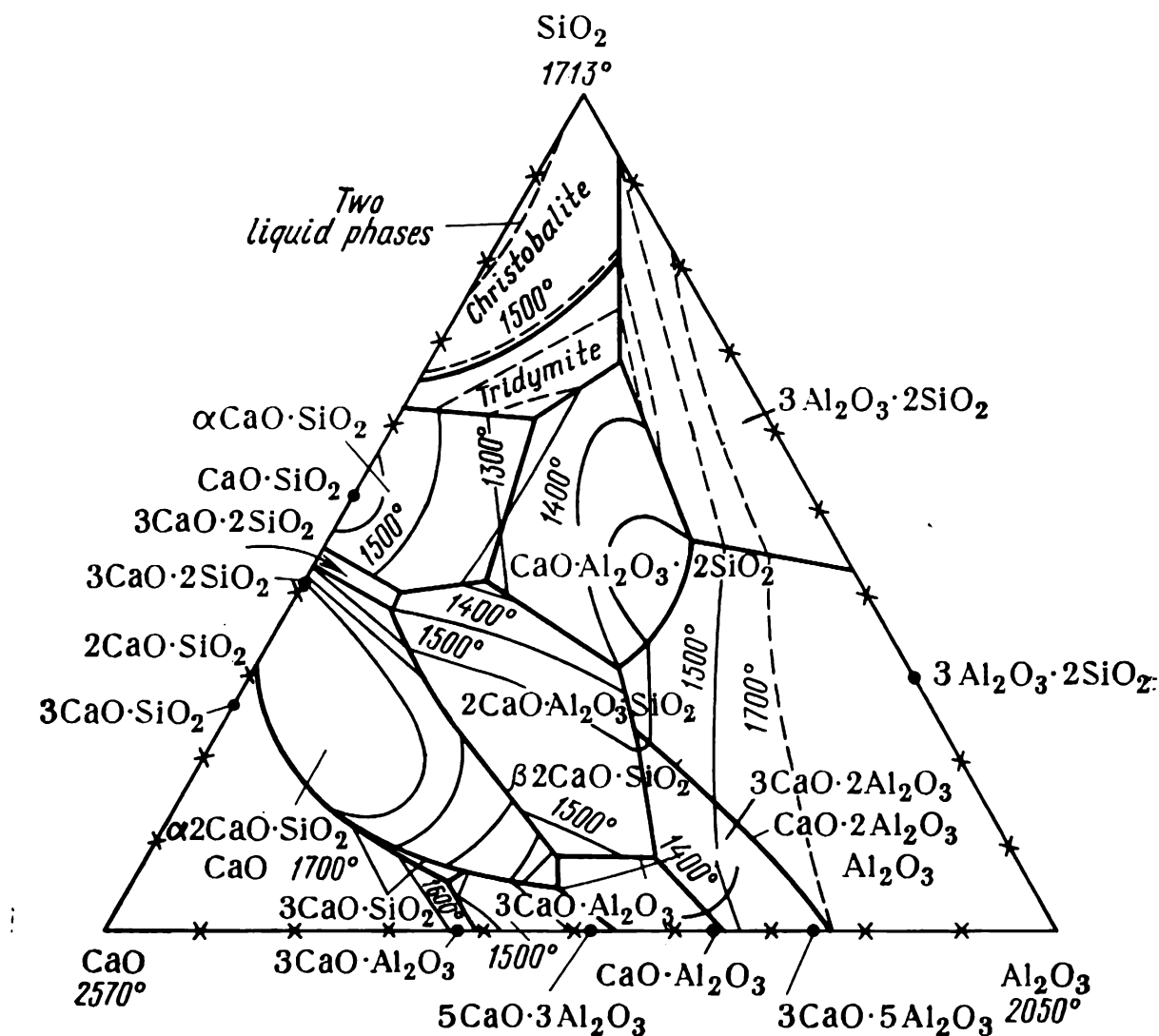


Fig. 45. Phase diagram for the  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$  system

recorder registers the difference in their temperatures,  $\Delta t$ , as a function of either the temperature of the sample or of the heating time. The curve obtained is known as a thermograph. The recorded differential curve,  $\Delta t - t$ , shows the points where a phase transformation occurs. From the endothermic and exothermic effects given by the heating curves (in temperature—time, temperature difference—temperature, etc. coordinate systems) reactions in a heated mixture can be discovered. By comparing thermographs of new compounds formed when the glass is cooked, using additional information obtained in petrographic and X-ray structural investigations, the mechanism of reactions in heated mixtures has been determined.

As an example, in Fig. 46 a curve is given for the heating of a mixture of  $\text{Na}_2\text{CO}_3$ ,  $\text{CaCO}_3$  and  $\text{SiO}_2$ , which corresponds to the lime-soda charge used most widely in making glass. The heating curve gives the difference between the temperature of the mixture being studied and that of a standard substance (usually calcined  $\text{Al}_2\text{O}_3$  or  $\text{MgO}$ ). The minima and maxima of the heating curve result from endothermic and exothermic heat effects of reactions or phase

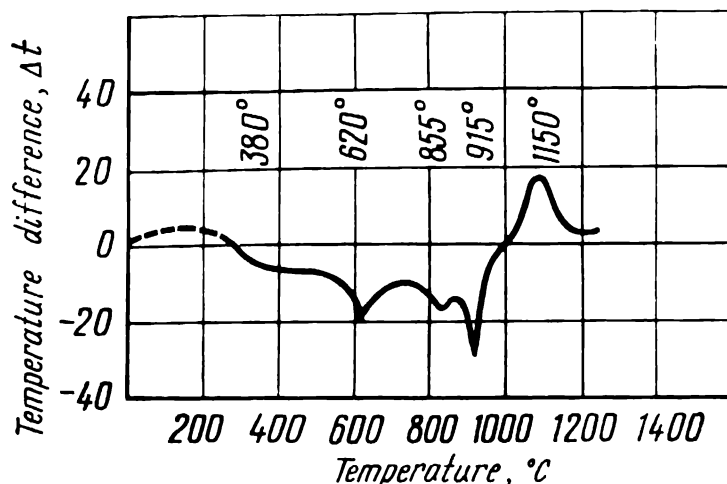
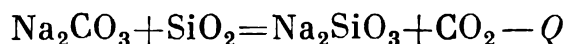


Fig. 46. Thermograph of a  $\text{CaCO}_3$ - $\text{Na}_2\text{CO}_3$ - $\text{SiO}_2$  mixture

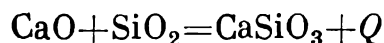
transitions. The decrease in the rate of the temperature rise at  $380^\circ\text{C}$  corresponds to liberation of  $\text{CO}_2$  from the charge when the following reaction begins



This reaction proceeds mainly at higher temperatures ( $700$ - $900^\circ\text{C}$ ). The endothermic effect at  $620^\circ\text{C}$  results from formation of the double salt  $\text{CaNa}_2(\text{CO}_3)_2$  and evolution of carbon dioxide by the reaction



The endothermic effect at  $855^\circ\text{C}$  is caused by the melting of soda ash, and that at  $915^\circ\text{C}$  by dissociation of limestone. The exothermic effect in the temperature interval of  $1010$  to  $1150^\circ\text{C}$  is a result of the exothermic reaction



Complete or partial melting of a silicate mixture followed by cooling of the molten mass leads to formation of a *glass (vitreous) phase*. Its presence in the final product (ceramics) gives it high strength by binding the separate minerals into a solid monolithic mass. In making glass, glazes and enamels the aim of the technological process is to produce a substance in the vitreous state.

*Glasses* are amorphous bodies produced by supercooling a non-metallic molten mass, which retains its liquid structure but acquires

the mechanical properties of a solid as a result of a gradual increase in its viscosity; the transition from the liquid (molten) state to the glass state is reversible.

The property of silicate molten materials to form glasses when cooled results from the presence of the basic structural element of silicates—the tetrahedral group  $\text{SiO}_4^{4-}$  which is capable of forming three-dimensional spatial lattices. The ability to transform into a glass state under certain conditions is a property not only of silicates, but also of boric anhydride, phosphates and sulphur. The glass state, which occupies an intermediate position between the solid state and the liquid state, has a number of specific features.

1. In contrast to crystalline systems glass is isotropic, i.e. its properties are uniform in all directions.

2. The marked dependence of the properties of the material on its composition is an important feature of glass. Some properties of glasses (specific heat, heat conductivity, density) follow the additivity rule, i.e. their value can be computed as the sum of the values for the individual substances of the glass composition. The influence exerted by each oxide component on the properties of a glass has been determined with high accuracy. Thus, for instance, silicon dioxide raises the chemical and thermal stability of a glass, and also its strength, but lowers the expansion coefficient; boric anhydride increases the refractive index and chemical stability of a glass and lowers its capacity to crystallize, etc.

3. A glass possesses higher internal energy than a crystalline substance of the same composition and because of this it is less stable. Glass crystallization is, therefore, accompanied by evolution of heat.

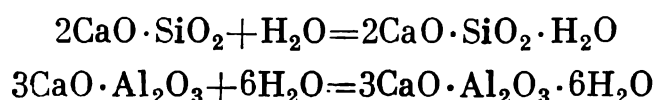
4. The capability of continuous transformation from the molten state to a solid one and vice versa is a property of the glass state; the solidification process does not involve formation of a new phase. The transition from liquid phase to solid phase and the reverse produce a continuous change in physicochemical properties.

*Colloid chemistry processes* are very important in silicate technology. During the formation of ceramic and refractory articles, in enriching clays and processing raw-material slurries in making cement, the material undergoing treatment is in the form of clay suspensions of various concentrations. To be able to use cements in structural practice and in industry the behaviour of the various components of the cement in a mix with water must be known. The binding properties of cements are based on the ability of silicates and aluminates of calcium to unite with water, and form high-strength crystals. Tri-calcium silicate hydrolyzes, according to the equation





Hydration of di-calcium silicate and tri-calcium aluminate takes place in the following way



The mechanism of setting and hardening of a cement which has been mixed with water can be represented in the following way. First, soluble compounds dissolve in water and form saturated solutions. During the second stage, colloid, jelly-like, low-solubility hydrosilicates, hydroaluminates and hydroferrites of calcium are formed (by the reactions given above), together with calcium hydroxide. During this period the mass is plastic and can easily be shaped. In the third stage, crystallization occurs within the jelly-like mass, with the various newly-formed colloids crystallizing at different rates. The calcium hydroxide and the hydroaluminate of calcium crystallize first. As a result of formation of crystals throughout the dough-like mass it solidifies, but it does not as yet possess high strength. This stage is known as setting of the cement.

The characteristic features of the following stage of hardening are closer packing; crystallization of the mass of the gel, which consists of hydrosilicates of calcium; drying of the mass, and an increase in its strength due to intergrowth and intertwining of the crystals. The most important of the phenomena which result in the increase in the mechanical strength of a cement is crystallization of the mineral that solidifies at the highest rate, i.e. of tri-calcium silicate, and the rate of increase in strength of the cement rock depends on the content of this component in the clinker.

### 3. The Manufacture of Portland Cement

Of all the various cements Portland cement is manufactured on the largest scale (on the average about 50% of the overall cement output). Portland cement is made from relatively available and cheap raw materials, articles made of such cement possess high strength, complete resistance to air and high frost resistance, they harden rapidly both in air and in water. Portland cement is a mixture of minerals: tri-calcium silicate,  $3\text{CaO} \cdot \text{SiO}_2$ , di-calcium silicate,  $2\text{CaO} \cdot \text{SiO}_2$ ; tri-calcium aluminate,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ ; tri-calcium alumina ferrite,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ ; unbonded calcium oxide,  $\text{CaO}$ , and magnesium oxide,  $\text{MgO}$ .

The schema and equipment used in making Portland cement are typical for the manufacture of the majority of cements. Portland cement is made by heating a carefully composed mixture of clay and calcium carbonate to the sintering point (the maximum firing temperature is 1400-1450 °C), followed by fine crushing of the sintered mass, which is called clinker. The ratio of the basic minerals

in Portland-cement clinker (per cent by weight) varies within the following limits:  $3\text{CaO} \cdot \text{SiO}_2$  42-60%;  $2\text{CaO} \cdot \text{SiO}_2$  15-35%;  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  5-14%;  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$  10-16%. In commercial practice the charge composition is calculated from the required percentage ratios of the basic oxides in the clinker. These ratios are called modules—the silicate module  $n$  and the alumina module  $p$ .

$$n = \frac{\% \text{SiO}_2}{\% \text{Al}_2\text{O}_3 + \% \text{Fe}_2\text{O}_3} \quad (5.1)$$

$$p = \frac{\% \text{Al}_2\text{O}_3}{\% \text{Fe}_2\text{O}_3} \quad (5.2)$$

$$\text{KS} = \frac{(\text{CaO}_{\text{overall}} - \text{CaO}_{\text{free}}) - (1.65\text{Al}_2\text{O}_3 + 0.35\text{Fe}_2\text{O}_3 + 0.7\text{SO}_3)}{2.8(\text{SiO}_{2\text{overall}} - \text{SiO}_{2\text{free}})} \quad (5.3)$$

The most important characteristic of the mineral composition of a Portland-cement clinker is the coefficient of saturation of the silica with lime, KS, expressing the ratio of the amount of lime remaining in the clinker after formation of  $2\text{CaO} \cdot \text{SiO}_2$ ,  $3\text{CaO} \cdot \text{Al}_2\text{O}_3$  and  $\text{CaSO}_4$  to the amount of lime necessary for combining with the silica present to form  $3\text{CaO} \cdot \text{SiO}_2$ .

From the desired module and KS values and data obtained by chemical analysis of the raw materials—limestone and clay, their ratio by weight in the charge is computed. For Portland cement the coefficient of saturation lies between 0.8 and 0.95. The lower the KS value, the higher will the content of  $2\text{CaO} \cdot \text{SiO}_2$  in the clinker be and the lower the activity of the cement.

The manufacture of Portland cement consists of two independent processes: (a) making the intermediate product—the clinker, which includes preparing the mixture of raw materials and firing it, and (b) crushing the clinker together with admixtures, storing and packing the Portland cement.

There are two methods for preparing the mixture of raw materials—a wet method and a dry method; correspondingly, dry and wet processes for manufacturing Portland cement are distinguished.

The specific feature of the wet process is that the raw materials are prepared in water, whereas in the dry process the materials are ground and mixed dry. At present the wet process is the most often used in the USSR and all over the world.

A *flow diagram* of the wet process for manufacturing Portland cement is given in Fig. 47. The limestone is disintegrated in crushers and the crushed limestone is fed to a tube mill where the limestone and the clay, introduced as a slurry from a clay mixer, are simultaneously subjected to fine grinding. From the mill the raw-material slurry is moved to a reinforced-concrete reservoir (slurry basin), where it is continuously stirred with mechanical mixers, or pneumatically. The slurry basins where the raw-material mixture is stored are used also for correcting its composition, i.e. slurries of different

chemical compositions are mixed to obtain the necessary component ratio.

The raw materials are fired in rotary-drum kilns. The kilns are heated using powdered coal, gas or fuel oil, with the fuel burned inside the kiln. The raw-material slurry is fed to the kiln from a horizontal slurry basin and moves through it countercurrent to the hot, gaseous combustion products. Their interaction results in the successive processes of water evaporation, mineral dehydration, limestone

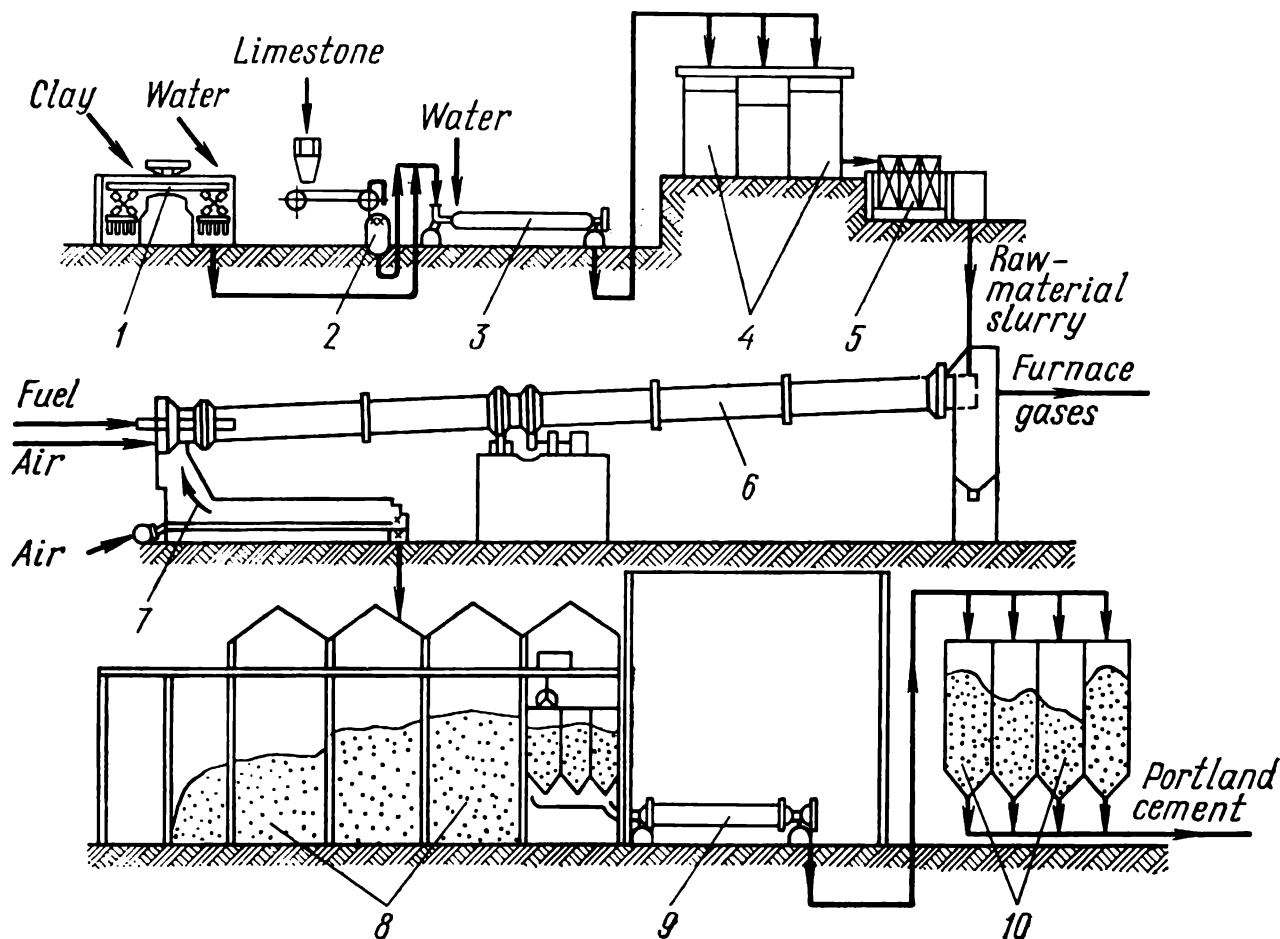


Fig. 47. Flow diagram of Portland cement manufacture by the wet process:

1—clay mixer; 2—hammer crusher; 3—raw-material mill; 4—correcting slurry-basins; 5—horizontal slurry-basins; 6—rotary drum kiln; 7—grate cooler; 8—storehouse; 9—cement mill; 10—cement silos

dissociation and chemical reactions between the basic oxide formed,  $\text{CaO}$ , and the components of the clay— $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ . In the sintering zone the cement clinker is finally formed at  $1450^\circ\text{C}$ . The clinker is cooled with cold air in grate coolers to a temperature of  $50\text{--}60^\circ\text{C}$ . In these coolers, which are located below the kiln, the air is passed up through a bed of clinker particles uniformly distributed on a bar grating. The air then flows to the kiln for combustion of the fuel. The clinker is transferred from the coolers to the storehouse, where it is kept for a certain time for slaking (hydration) of free lime and binding it using hydraulic admixtures. The aged clinker, together with hydraulic or inert admixtures and gypsum,

added to control the setting time, is ground in cement ball-mills. Cement is stored in reinforced-concrete silos, containing air nozzles at the bottom through which air is forced when the cement is being discharged, to loosen it. Cement is delivered to consumers in bulk, in lorry- or railway cement-tanks, or packaged in paper, multilayer bags.

Various additives are mixed into cements to give them specific properties or to lower their cost—hydraulic admixtures, containing active silica, which raise the resistance of a cement to the effects of water and promote its hardening under water; plasticizing, surface-active substances, which increase the elasticity and adhesive properties of the cement; inert fillers (sand, limestone, dolomite); acid-resistant components (andesite, granite); admixtures which govern the setting rate (gypsum), etc. An especially important additive is amorphous silica, whose hydraulic effect is a result of its binding of free  $\text{Ca(OH)}_2$  to form a calcium hydrosilicate, and also through significantly increasing the density of the concrete. This leads to increased resistance of the concrete to water and lowers corrosion by carbon dioxide dissolved in the water.

**Puzzolana Portland cement and Portland slag cement.** To save on Portland cement—a universal but expensive cement—mixed cements are made, which can only be used with certain limits. Puzzolana cements are finely-ground mixtures of Portland-cement clinker with hydraulic admixtures added in amounts from 20 to 50%. The hydraulic ingredients may be porous volcanic rock (puzzolanas), sedimentary minerals consisting mainly of amorphous silica (diatomite, tripoli), or silica-containing industrial waste materials. Puzzolana cements are mainly used as special cements for making underwater and underground structures, but they cannot be used where there are large changes in the temperature. Puzzolana cements harden very slowly.

Portland slag cement is a mixture of Portland-cement clinker and finely ground metallurgical slag, most often blast-furnace slag. Portland slag cement has high water resistance and it is used in concrete and reinforced-concrete structures which are not subjected to large temperature and moisture variations. Partial replacement of cement clinker by such waste products as slags, which have already been subjected to thermal treatment in metallurgical furnaces, considerably lowers the cost of a cement.

## 1. Introduction

Metallurgy originated in very ancient times. Iron, copper, silver, gold, mercury, tin and lead were known to man and were used by him at the very beginning of the development of society. Tin and lead, which can be reduced relatively easily from their oxides, were the first metals to be won. But these metals are not suitable for making tools and arms from them. When man learned how to alloy copper with tin, this was the beginning of a new age in the history of mankind, called The Bronze Age. Improved smelting furnaces made it possible to produce iron from its ores; iron replaced bronze and in the form of cast iron and various iron alloys became the basis for the growth and development of industry, transportation and agriculture. Up to the beginning of the 18th century only the metals gold, silver, copper, mercury, iron, lead, tin, antimony and bismuth were known to man. Production of such metals as aluminium, nickel, magnesium, chromium, manganese and others began only at the end of the 19th and beginning of the 20th century.

Russian scientists played an important part in developing metallurgy to the stage where it has become a science; they developed new methods for manufacturing metals.

**A classification of metals\*.** Metals make up a major part of the elements of the Mendeleyev Periodic System. Commercially metals are classified by other properties than those lying at the basis of the Periodic System of the elements. However, up to the present no strict, scientific classification of the metals has as yet been developed. Classifications used in industrial practice are based on such properties of the metals as their availability, applications, physical and, to some extent, chemical properties.

Metals are divided into *ferrous* and *non-ferrous* ones. The ferrous-metals group includes iron, manganese, chromium and their alloys; all the rest are non-ferrous metals.

Non-ferrous metals are subdivided into four groups: (1) heavy metals: copper, lead, tin, zinc and nickel; (2) light metals: alumi-

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\* The classification given is not universally accepted, it is not perfect and does not correspond to the modern state of metallurgy; at present a new classification of metals is being developed.

nium, magnesium, calcium, potassium and sodium; often barium, beryllium, lithium and other alkaline and alkaline-earth metals are included in this group; (3) precious or noble metals: platinum, iridium, osmium, palladium, ruthenium, rhodium, gold and silver; (4) rare metals: (a) high-melting metals: tungsten, molybdenum, vanadium, tantalum, titanium, zirconium and niobium; occasionally cobalt is also included in this group; (b) light metals: strontium, scandium, cesium, rubidium and others; (c) scattered metals: germanium, gallium, thallium, indium and rhenium; (d) rare-earth metals: lanthanum, yttrium, hafnium, cerium, scandium and others; (e) radioactive metals: thorium, radium, actinium, protactinium, polonium, uranium and the transuranium elements. The so-called small metals—antimony, mercury, and bismuth—are often separated from the rare metals into a distinct group.

Metals in the solid state are crystalline substances, whose atoms are arranged in a definite pattern and form a so-called crystal lattice. The structure of a metal depends on the shape, size and respective location of the crystals in it. The strength and other engineering properties of a metal are to a very large degree determined by the metal structure.

The crystals of the most important metals have the form of (a) a centred cube (crystals of  $\alpha$ -Fe, Cr, V, Mo, W, K, Na and others with a coordination number of 8); (b) a face-centred cube (crystals of  $\gamma$ -Fe, Ni, Co, Cu, Al, Au, Ca and others with a coordination number of 12); (c) a hexagonal form, with the densest packing (crystals of Zn, Mg, Cd, Ti and others with a coordination number of 12). In metals allotropic transformations often occur, i.e. a metal can have various crystal forms, depending on the conditions during crystallization and cooling of the solid (polymorphism). Thermal treatment of metals (e.g. annealing, tempering) is based on their capability to undergo polymorphic transformations.

**Alloys.** Metals can form alloys, which are highly important in technology. Alloys are solid substances produced by simultaneous melting of several simple substances (elements) or various chemical compounds.

In general, only the alloys of crystalline substances are of practical interest. The term “alloy” is therefore usually meant to apply to crystalline substances, most often to metals. Chemically stable alloys should have a uniform structure, since crystals of different types form electrochemical couples which when acted on by reagents cause corrosion of the metal. The uniformity of a metal alloy depends to a very large degree on the crystal lattices of the initial constituents. Depending on the number of elementary substances (constituents) in the molten mass alloys are classed as binary, ternary, quaternary, etc. The binary alloys have been most thoroughly studied.

A characteristic feature of all alloys is a certain degree of interaction between the fused substances. In the liquid state all the components are completely mixed to form a uniform liquid. In the solid state there is a uniform crystalline mixture of the components, their solid solutions or their chemical compounds. Each of the three types of interaction of components mentioned corresponds to a specific form of crystallization and a definite structure. The alloys of iron are the most important.

**Iron.** Iron has several allotropic forms: alpha-iron ( $\alpha$ -Fe), gamma-iron ( $\gamma$ -Fe) and delta-iron ( $\delta$ -Fe). Alpha-iron ( $\alpha$ -Fe) possesses magnetic properties, is stable at temperatures below 910 °C and has a cube-centred crystal lattice. The solubility of carbon in it is very low: 0.02 per cent at a temperature of 723 °C and 0.006 per cent at room temperature. The solid solution of carbon in  $\alpha$ -Fe is known as ferrite. At 910 °C  $\alpha$ -iron transforms into  $\gamma$ -iron, with a face-centred cubic crystal lattice. Gamma-iron ( $\gamma$ -Fe) can dissolve carbon in larger amounts than  $\alpha$ -Fe: 0.8 per cent at 723 °C and 2 per cent at 1130 °C. The solid solution of carbon in  $\gamma$ -Fe is called austenite.

At 1401 °C  $\gamma$ -iron transforms into  $\delta$ -iron, which also crystallizes as centred cubes and this form is retained up to the melting point of iron, 1539 °C. The chemical compound of iron with carbon (iron carbide)  $\text{Fe}_3\text{C}$  is called cementite. Chemically pure iron is a silvery white substance with a density of 7890 kg/m<sup>3</sup>. It has high heat conductivity, electrical conductivity, magnetic permeability; it is highly plastic, forms well when forged, stamped or rolled, and can easily be welded.

Many diverse alloys which are widely used in industry are based on iron. The consumption of iron and its alloys at present represents 92-93 per cent of the total consumption of metals. Iron alloys containing carbon are extremely important.

Fig. 48 is a phase diagram which shows the phase and structural transformations in iron-carbon alloys with changes in the temperature. All iron-carbon alloys are liquid at temperatures lying above curve *ACD*. This curve shows how the temperature at which crystallization of the alloys begins depends on the carbon content. Below curve *AECF* all the alloys are in the solid state. The eutectic iron-carbon alloy contains 4.3 per cent carbon, solidifies at 1130 °C and is known as ledeburite; it consists of a mechanical mixture of grains—*austenite* and *cementite*—above 723 °C, and *perlite* and *cementite* below 723 °C. The alloy with a carbon content of 6.67 per cent is *cementite*,  $\text{Fe}_3\text{C}$ . Point *E* on the diagram (at 1130 °C) corresponds to maximum solubility of carbon in solid iron (two per cent). Point *O* at 723 °C and a 0.83 per cent carbon content is called an *eutectoid point* since, in contrast to a eutectic point, an alloy is formed here not from liquid metal, but from a solid *austenite* solution, when  $\gamma$ -iron is transformed into  $\alpha$ -iron. This alloy, similar to a eutectic,

has a fixed composition (0.83 per cent C) and minimum temperature of formation (723 °C). It consists of a mixture of grains of cementite and ferrite and is known as perlite.

When the alloys are cooled, at 723 °C  $\gamma$ -iron is transformed into  $\alpha$ -iron with liberation of cementite. In this way, all the austenite decomposes into the mechanical mixture—perlite. On heating the

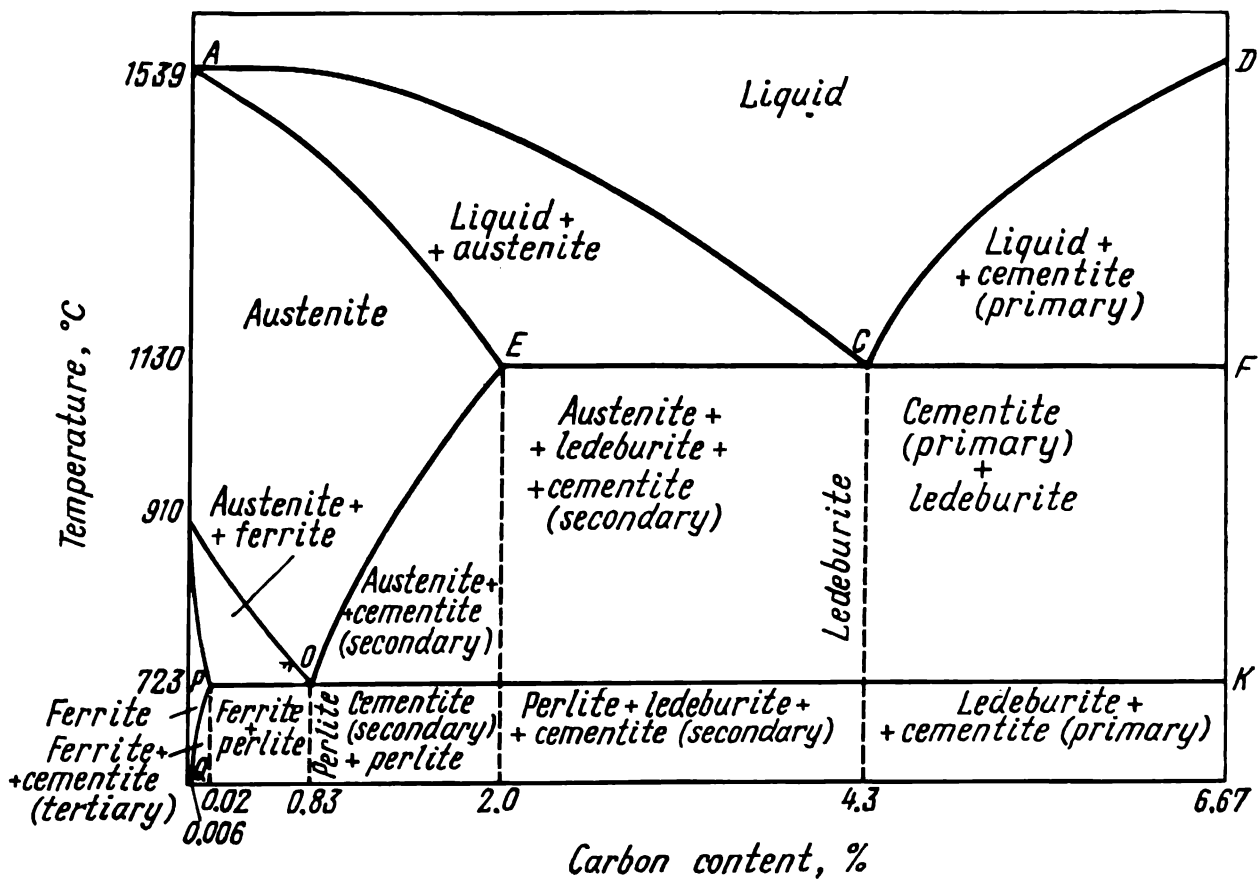


Fig. 48. Phase diagram for the iron-cementite system

reverse process occurs. At 723 °C  $\alpha$ -iron changes into  $\gamma$ -iron in which the carbon of the alloy dissolves to form a solid solution, i.e. austenite.

The *PK* line is called the line of perlite, or austenite, transformation. The diagram shows the structure of all the intermediate alloys. Alloys with a carbon content of up to 2.0 per cent are known as steel, alloys with a higher carbon content, as cast iron. If a large part of the carbon in a cast iron is chemically combined with the iron in the form of  $\text{Fe}_3\text{C}$ , it is called white cast iron. If molten cast iron is slowly cooled part of the  $\text{Fe}_3\text{C}$  decomposes, and carbon (graphite) is liberated. This is called gray cast iron. In such a case the phase diagram is slightly different. White cast iron is harder, but it is more brittle and therefore usually is not subjected to machining and is used in making steel. Gray cast iron is softer, less brittle and can easily be machined.



**Ores and ore-processing methods.** Ores are materials mined from the earth which contain valuable metals in such amounts that they can be profitably separated at the modern level of technical and economics conditions. Most often an ore is an aggregate of different minerals, and the mineral which contains the desired metal is called the ore and all the others—the gangue. According to the metal made from them, they are designated as iron, copper, lead, copper-nickel, lead-zinc, etc. ores. An ore from which several metals are obtained is often known as a polymetal one. According to the composition of the minerals in the ores, they are classed as sulphide, oxidized or native. Ores in which the metal to be separated is in the form of an oxide or other oxygen-containing minerals—silicates, carbonates, etc.—make up the oxidized class. Copper, lead and zinc ores are predominantly of the sulphide group—the metal is combined with sulphur ( $\text{CuFeS}_2$  chalcopyrite,  $\text{PbS}$  galenite,  $\text{ZnS}$  sphalerite, etc.). Iron ores belong to the oxidized-ore group.

Native ores are those which contain naturally occurring fused metals. Gold ores belong to this category. The gangue, which is part of the ore, usually consists of silica, silicates, alumina, barite, pyrites, oxides of iron, etc. Ores are considered to be acidic if the gangue consists primarily of silica ( $\text{SiO}_2$ ), basic when the gangue is made up mainly of  $\text{CaO}$ ,  $\text{MgO}$  or  $\text{FeO}$ , and neutral if the ratio of basic compounds and silica approximately corresponds to their content in the slag obtained when the ore is processed.

Whether it is worthwhile to process a given kind of rock and, consequently, whether it should be considered an ore, depends on a number of factors, but the determining one is usually the content of metal in it. Thus, for example, at the existing level of technical development ores should contain, approximately, not less than 30 per cent Fe for iron ores, 3 per cent Zn for zinc ores, 0.5 per cent Cu for copper ores. Depending on the composition of an ore and the content of the desired metal in it, it may be used in the metallurgical process directly or may first be subjected to beneficiation.

To obtain the metal from the ore the gangue must first be removed, after which the minerals of the ore are decomposed to separate the metal from the elements with which it is chemically combined. These processes for treating ores are known as metallurgical processes. To increase the rate of the chemical reactions involved metallurgical processes are carried out either at high temperatures, in which case they are called pyrometallurgical ones, or the ores are treated with aqueous solutions of reagents; these latter processes are called hydrometallurgical ones. Typical operations in pyrometallurgy are calcining, melting and distilling, and in hydrometallurgy—leaching and precipitating from solutions, and, in particular, electrolysis of solutions.

Metals are reduced in pyrometallurgical processes mainly using coke and carbon monoxide produced from the coke directly inside the furnace by incomplete combustion of carbon.

Part of the coke used in a blast furnace for making pig iron can be replaced with natural gas, coke-oven gas, fuel oil or pulverized coal. The impurities produced are removed from the principal metal by converting them into a slag in the form of their oxides and salts, mainly low-melting silicates.

Ferrous metals—cast iron and steel of different grades—are obtained by pyrometallurgical methods. In manufacturing non-ferrous metals combinations of pyro- and hydrometallurgical processes are usually used. Thus, in manufacturing aluminium alumina is obtained from the ore by pyro- and hydrometallurgical operations, whereas the aluminium is made from the alumina by a pyrometallurgical process, i.e. by electrolysis of the molten material. The principal stages in obtaining copper from sulphide ores are of a pyrometallurgical nature, but the final operation of copper purification (refining) is usually carried out by electrolysis of an aqueous solution, i.e. by a hydrometallurgical process.

Many diverse processes and technological methods are employed in the metallurgy of rare metals, whose content in the ores usually comprises only a fraction of a per cent. In rare-metal metallurgy all the basic methods are employed which are used for obtaining metals in the other fields of ferrous and non-ferrous metallurgy and, besides these, a number of the typical operations of the chemical technology of inorganic salts. The first stage in the production process usually consists of various operations for concentrating the raw material. The next stage comprises decomposition of the concentrate obtained in the beneficiation stage by calcination, interaction with gases (chlorine, sulphur dioxide, etc.) or processing with liquid solvents (acids, alkalies, etc.). Usually the metal which is being won is transferred to a solution, from which the oxide or a salt of the rare metal is separated by precipitating a low-solubility compound or by crystallization.

In the final stage a pure metal or an alloy is prepared by a process of electrolysis of a solution or a fused electrolyte, cementation, thermal dissociation, or reduction with carbon or hydrogen. For carrying out this stage metallothermics may also be employed, i.e. reduction of the metal from its oxides with silicon, ferrosilicon, aluminium or other substances which form oxides more stable than the oxide of the metal being manufactured.

Powder metallurgy—reduction of a powder to form a metal from its oxide—is utilized in manufacturing high-melting metals (tungsten, titanium, etc.). High-melting alloys are made by compressing powders of the metals; this is followed by sintering in electric furnaces. The sintering temperature of a powder is usually at about  $\frac{2}{3}$  of

the melting point of the metal. The melting point of a powder mixture is in some cases lower than the melting point of the pure metals. Consequently, powder-metallurgy techniques lower the temperature necessary for making high-melting alloys, and this is an important advantage of the powder-metallurgy method. Powder-metallurgy techniques can also be employed in manufacturing ferrous metals.

## 2. The Manufacture of Pig Iron and Steel

Of the furnaces of many types which are employed in making metals those used on the widest scale are shaft (blast) furnaces, baths (open-hearth, Bessemer converter, and crucible) and electric furnaces (arc- or induction-heated). Modern blast furnaces (see Part I, Fig. 73) are units of large capacity whose volume measures up to 5000 cu m. Such a furnace consumes up to 25 000 tons of the charge per day and continuously discharges through 4 taps up to 13 000 tons of pig iron per day (4 million tons per year). To intensify the operation of the shaft furnace natural gas and fuel oil are added to the air blast which is enriched with oxygen (up to 30%) and also the pressure is raised to 2-2.5 atm. Mean coke consumption per 1 kilogram of pig iron produced in the USSR is from 0.45 to 0.55 kg.

An index of the operating efficiency is the ratio of carbon consumed,  $I_C$ , to the useful volume of the furnace:

$$I_C = \frac{C_c C + C_a Q_a}{100v} \quad (6.1)$$

$C_c$  being the carbon content of the coke, %;  $C_a$  the carbon content of carbon-containing additives, %;  $C$  the amount of coke consumed, tons per day;  $Q_a$ —the amount of carbon-containing additive consumed, m<sup>3</sup> per day;  $v$ —the useful furnace volume, m<sup>3</sup>. The furnace operating intensity calculated using equation (6.1) has a value of 0.95-1.25 tons/m<sup>3</sup>·day.

The structure of the cost of pig iron is:

Raw materials	30-40
Coke	40-55
Natural gas	2-4
Production costs	13-18
(including wages and salaries	0.3-0.7)

Transformation of pig iron into steel consists in reducing the content of carbon by oxidizing it, removing to the maximum possible degree sulphur and phosphorus and bringing silicon, manganese and other elements to the required amounts in the steel. The carbon can be oxidized in two different ways, by blowing oxygen through the molten pig iron in the Bessemer converter method, or by adding solid oxidizing agents to the molten pig iron (iron ore, scale, etc.)—

in the open-hearth method. By both methods the carbon is oxidized to its dioxide and monoxide, and such components as silicon and manganese are to a large extent transferred to the slag in the form of  $\text{SiO}_2$  and  $\text{MnO}$ . An excess of calcium oxide must be maintained in the slag to remove sulphur and phosphorus from the pig iron.

An *open-hearth furnace* (Fig. 49) is made up of its roof, front-, back- and side-walls, hearth and regenerators. There are holes

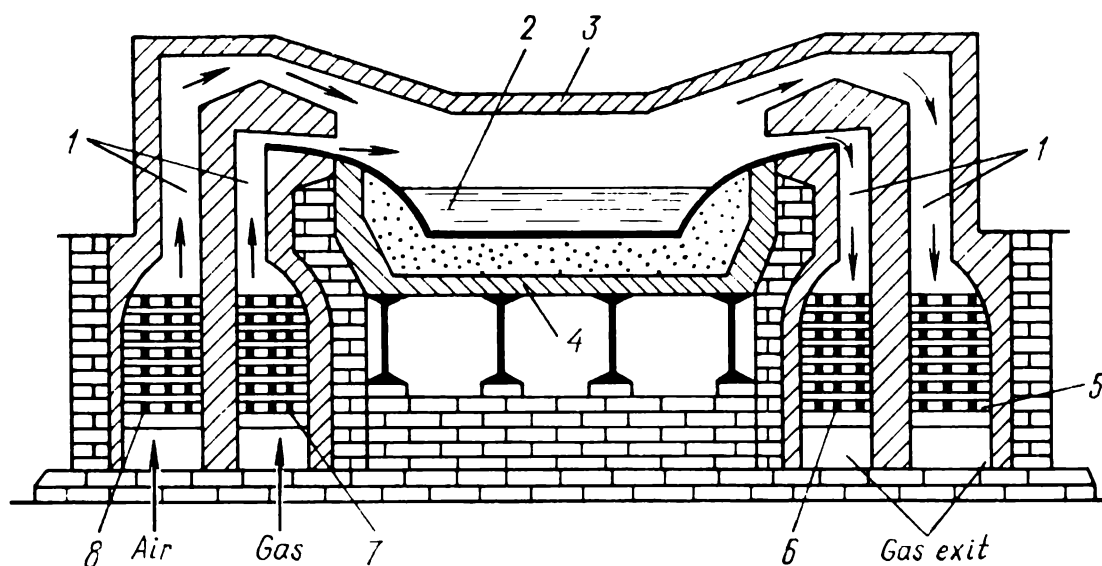


Fig. 49. Open-hearth furnace:

1—ducts through which gas fuel and air are fed and combustion products are withdrawn;  
2—operating space; 3—furnace roof; 4—furnace hearth; 5-8—regenerators

in the front wall through which the charge is introduced, in the back wall—for discharging the steel, and in the side walls—for supplying a gaseous fuel and air for its combustion to it, and also for removing the combustion products with a temperature of  $1600^\circ\text{C}$  to the regenerators. The regenerators are necessary to provide maximum utilization of the fuel. The temperature in the regenerators is given by

$$t = \frac{Q}{cM} \quad (6.2)$$

where  $Q$  is the excess heat of the combustion products,  $c$  the heat content of the combustion products,  $M$  their mass.

By replacing the air, or part of it, with oxygen the mass of the combustion products [see (6.2)] is lowered and in this way the temperature of the reaction is increased. The production capacity of large open-hearth furnaces has been raised to 1-1.5 million tons per year by intensive consumption of oxygen, speeding up the process of oxidizing impurities, providing a large driving force, rapid flow of the hot gases, and employing radiated heat to raise the mass transfer ( $k$ ) and heat transfer ( $\alpha$ ) coefficients.

The conditions in a two-bath furnace (Fig. 50) are quite specific: the free volume of one furnace is paired to that of another and the

excess heat of one bath is utilized in the neighbouring one, which makes it possible to do without regenerators for preliminary heating of the gas and air.

Growth in steel output is taking place mainly by building large capacity Bessemer converters with basic refractory linings. Smelting steel from pig iron (Fig. 51) to which steel scrap is added is carried

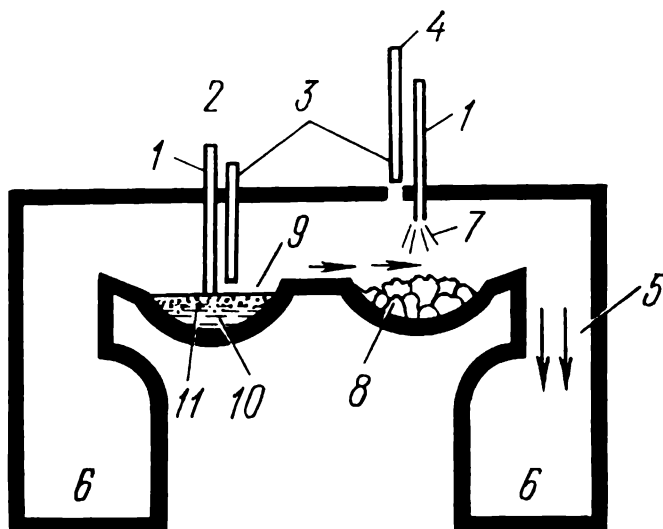


Fig. 50. Schematic diagram of a two-bath furnace:

1—fuel-oxygen tuyeres; 2—position of a tuyere during final stage; 3—tuyeres through which solids are blown in; 4—tuyere position in scrap-heating stage; 5—effluent gases; 6—slag ports; 7—flame; 8—scrap; 9—direction of gas flow; 10—steel; 11—slag

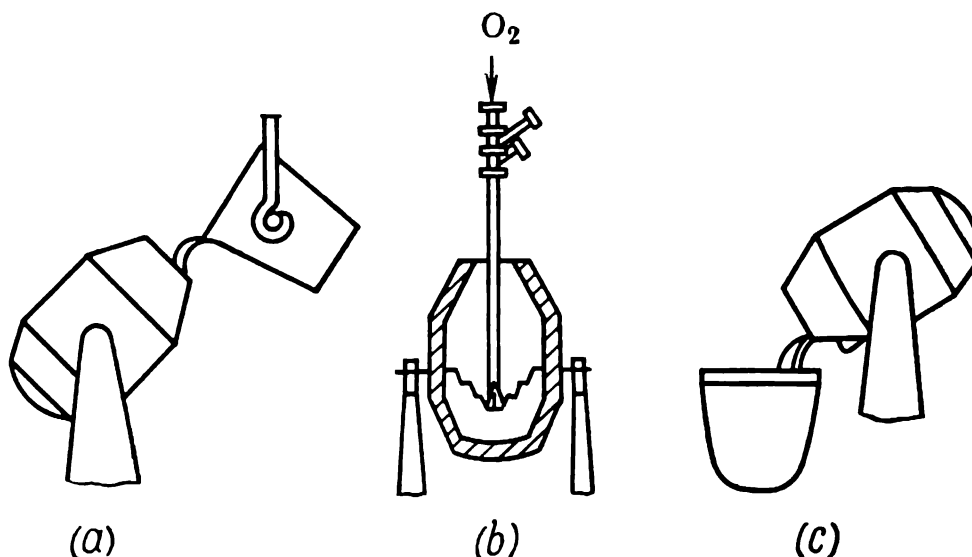


Fig. 51. The basic operations of oxygen-converter smelting:

(a)—loading; (b)—blow; (c)—discharge

out using several streams of oxygen (at a pressure of 9-14 atm) supplied through the top of the unit. The oxygen streams, with a content of 99.5%  $O_2$ , flow through the metal causing it to circulate and to mix with the slag. Oxygen is fed for a period of 14 to 24 minutes,

and at the end of the smelting operation the molten mass of steel is poured into a ladle.

Special types of high quality steels (rust proof, instrument, high temperature) and other steels for particularly important uses are only smelted in electric furnaces (arc or induction type). This is

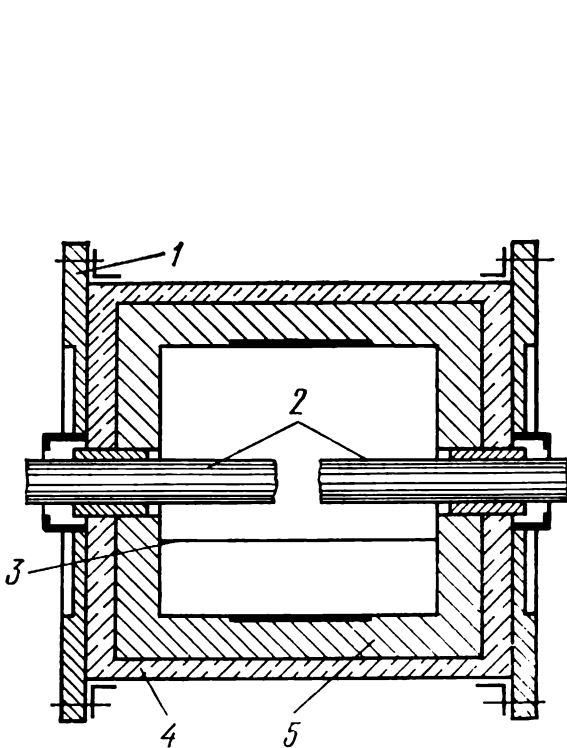


Fig. 52. Indirect-heat arc furnace:  
1—furnace shell; 2—electrodes; 3—level of metal in the furnace; 4—thermal-insulation layer; 5—lining

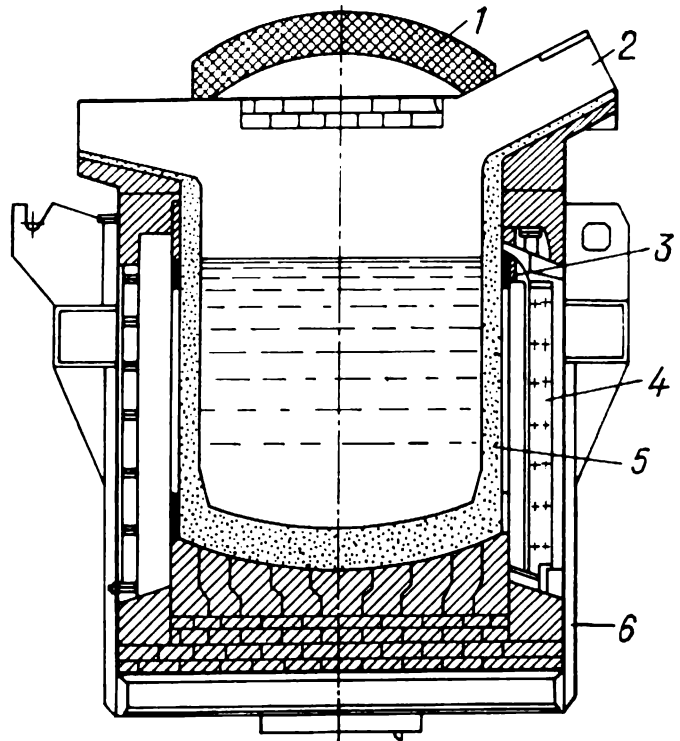


Fig. 53. Induction furnace without a core (for smelting steel):

1—furnace roof; 2—outlet trough; 3—water-cooled inductor; 4—magnetic shield; 5—furnace crucible; 6—casing

because in electric furnaces the temperature can be raised rapidly and can be closely controlled, introduction of impurities from fuel-combustion products is excluded, special types of admixtures can be melted by raising the temperature to as high as  $3000^{\circ}\text{C}$  and any desired type of metallurgical processing can be carried out by maintaining, as needed, an oxidizing, reducing or neutral medium or a vacuum in the gas phase.

*In arc furnaces* an electric arc between two electrodes is formed (Fig. 52) and the material is heated by radiation from the arc. In combination furnaces (see Part I, Fig. 81) heating is accomplished by means of an electric arc between the electrodes and the metal. In large electric furnaces the electrodes are lowered automatically at the same speed with which they burn and are continuously lengthened at the other end without interrupting furnace operation (see Part I, Fig. 83).

*In induction furnaces* a material which is a conductor of electricity is heated either by electric currents induced within it or by means

of a heater which uses induced electric currents. Induction furnaces are used in metallurgy for smelting and resmelting metals. Induction furnaces with an iron core imbedded in the material being heated or without such a core are employed. An induction furnace without a heating core (Fig. 53) has the form of a coil (the inductor) surrounding the metal (charge) contained in a crucible. Alternating current is passed through the inductor and it creates an alternating magnetic field, which in turn induces eddy currents in the metal charge, causing the heat needed for the process to be liberated.

### 3. The Manufacture of Copper

Copper is a metal which is used in industry on a broad scale. The pure metal has a light rose colour. Its melting point is  $1083^{\circ}\text{C}$ , boiling point  $2300^{\circ}\text{C}$ , and its density  $8.93\text{ g/cm}^3$ . The metal is very viscous, hammers and rolls well both when cold and hot. Copper is an extremely good conductor of heat and electricity and is second only to silver in this respect. At ordinary temperatures copper is not readily oxidized, but in the presence of  $\text{CO}_2$  and  $\text{H}_2\text{O}$  its surface becomes covered with a greenish coating of basic copper carbonate. Copper dissolves in  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$ . In the presence of air, water vapour and  $\text{SO}_2$  copper becomes covered with a dense green-gray film of its basic sulphate salt, which protects the metal from further corrosion. In the molten state copper absorbs  $\text{O}_2$ ,  $\text{SO}_2$  and other gases. Small amounts of Mn, Ni, Zn, Sn form solid solutions in copper and produce alloys which are harder and less viscous than the pure metal. The presence of Bi, Pb, Sn reduces its malleability. Copper is the basic material used in making wire, cables, current busses and other current-conducting parts of electrical devices. About 50 per cent of all copper manufactured is consumed by the electrical engineering industry. Impurities in copper reduce its electrical conductivity. The high heat conductivity of copper has led to its wide use for making diverse types of heat exchangers, coolers, radiators of internal combustion engines and other similar equipment.

Copper alloys of many different names depending on their composition are extensively employed in industry. Copper alloys containing zinc are called brasses, and their alloys containing tin are known as bronzes.

Copper ores serve as the raw material from which the metal is manufactured. Copper is present in nature in sulphide, oxidized, mixed and natural copper ores. The most important of these are the sulphide ores (approximately 80% of the total amount). The copper content of the ores lies between one and five per cent; ores which contain less than 0.5 per cent copper cannot be profitably processed at the present level of technical development.

Copper ores besides copper (1 to 6%) often contain other metals as well—zinc, lead, nickel, molybdenum and also selenium, arsenic, tellurium, thallium, gold and silver. Poor sulphide copper ores and complex ores are usually subjected to beneficiation by flotation, which produces concentrates containing 10-30 per cent copper. By selective flotation of complex ores lead-, zinc-, nickel- and other concentrates are also produced; these serve as raw materials from which the respective metals are made. In addition to copper ores industrial and domestic copper and copper-alloy scrap are used as raw materials for manufacturing copper. About 30 per cent of the total amount of copper produced is made from such secondary raw materials.

Two basic methods are used for winning copper from its ores and concentrates: a pyrometallurgical method and a hydrometallurgical one.

*The pyrometallurgical method* can be employed for processing sulphide, oxide and mixed ores. By this method concentrates of the noble metals can be obtained from the ore along with the copper. About 90 per cent of all the copper produced in the world is made by pyrometallurgical processes. The hydrometallurgical method is only employed for treating oxide ores, mainly ores with a low copper content, and also for processing native ores. In hydrometallurgical processes the noble metals are usually not recovered from the ore. This method has not come to be used on a wide scale in industry.

*The pyrometallurgical process of manufacturing copper* (Fig. 54) is based on fusing sulphide ores. Sulphide ores not only contain sulphides of copper, iron and other metals, but also gangue, consisting of oxides of silicon, aluminium, iron, calcium, etc. When such an ore is fused and allowed to stand the molten mass separates into two layers—the lower layer is a sulphide melt with a density of approximately 5 g/cm<sup>3</sup>, and the upper layer a melt of oxides with a density of approximately 3 g/cm<sup>3</sup>. The molten sulphides consist mainly of the sulphides of copper and iron; this material is called matte ( $\text{Cu}_2\text{S} \cdot n\text{FeS}$ ); the molten oxides make up the slag. The matte is an intermediate product, from which blister copper is made. It follows that the pyrometallurgical process consists of two main stages: (1) melting the ore to produce copper matte and (2) reprocessing the molten matte into blister copper by blowing air through it.

*Matte smelting* is carried out either in reverberatory or in shaft furnaces. The shaft furnaces have a water jacket around the lower part and are called water-jacket furnaces. Usually reverberatory furnaces, which are very similar to open-hearth furnaces, are used for melting concentrates and ore fines.

When the ore is to be melted in a reverberatory furnace it is rational to use preliminary roasting in which a large part of the iron sulphide is oxidized to ferric and ferrous oxide, and copper is



left in the form of  $\text{Cu}_2\text{S}$ . The subsequent smelting of preroasted ore (with the sulphur remainder comprising about ten per cent) in a reverberatory furnace yields a matte with a high copper content.

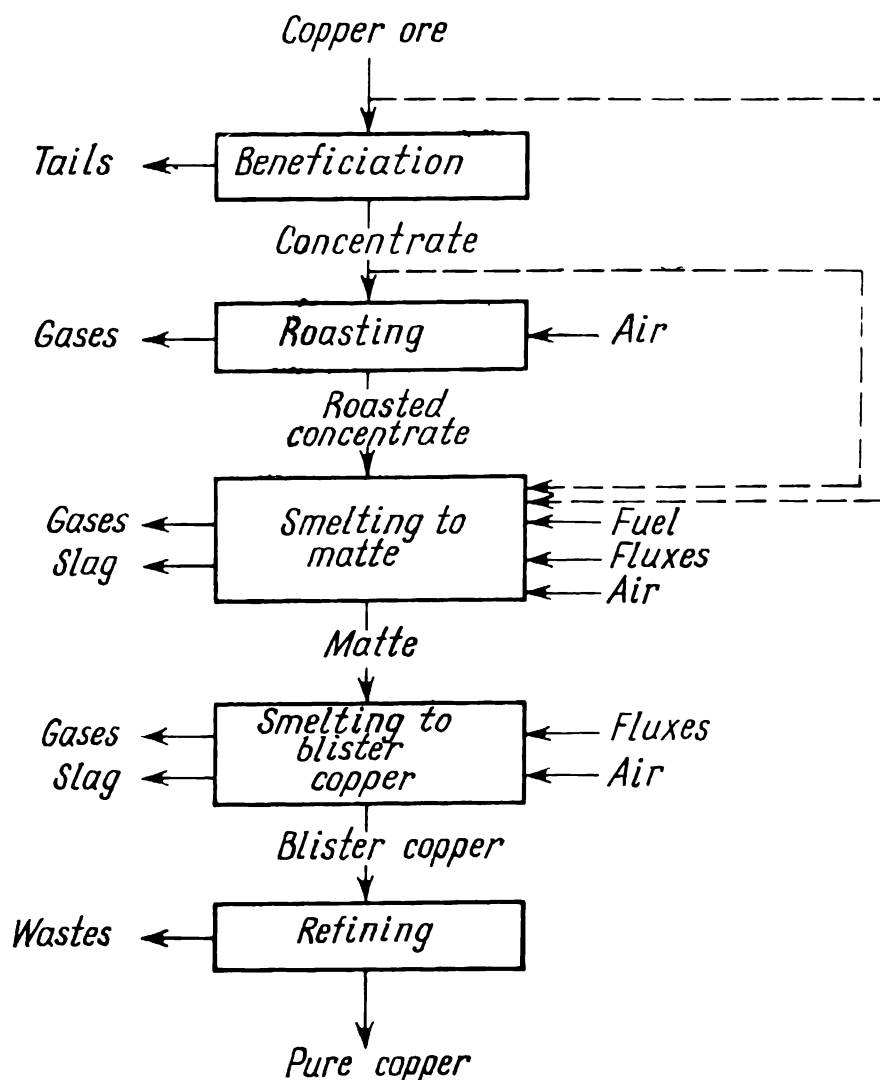
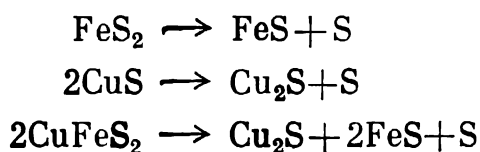
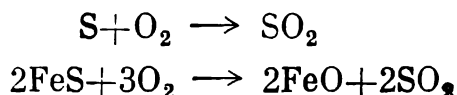


Fig. 54. Schematic diagram of the pyrometallurgical process for making copper

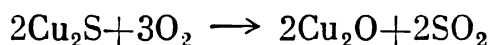
During the operation of roasting copper ores or their concentrates a number of processes take place



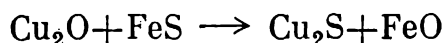
These processes of dissociation in the roasting furnace are accompanied by oxidation of sulphur and iron sulphide with the oxygen of the air



Cuprous sulphide is also oxidized, by the following reaction



However, actually only iron sulphide is oxidized, since the cuprous oxide formed reacts with iron sulphide and is reconverted to the sulphide



Copper ores are roasted in fluidized-bed or in multihearth furnaces of the same type as those used for roasting pyrite. The roaster gas produced containing  $\text{SO}_2$  is utilized; sulphuric acid is made from it.

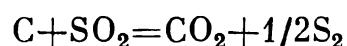
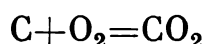
The roasted copper concentrates are melted in reverberatory furnaces to produce matte with flux added to convert the gangue into slag. The flux contains enough silica and limestone to produce together with the gangue and the ash of the fuel a low-melting mixture and a molten slag of low density and viscosity. Reverberatory furnaces are heated using either fuel oil or coal dust. The temperature in the smelting furnace reaches 1550-1600 °C.

Matte formation is an extremely complex process. The roasted concentrate introduced into the smelting furnace contains  $\text{Cu}_2\text{S}$ ,  $\text{FeS}$ ,  $\text{FeO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{CaO}$ ,  $\text{SiO}_2$ . At the high temperature in the furnace the components of the mixture with the lowest melting point,  $\text{FeS}$  and  $\text{Cu}_2\text{S}$ , melt first, and the molten sulphide mixture formed, the matte, flows down to the bath at the bottom of the furnace, from which it is periodically removed through taps in the side wall when it accumulates. The oxides of the gangue at 1030-1060 °C form low melting  $\text{FeO-SiO}_2\text{-CaO}$  eutectics. The primary molten body of silicates flows down into the furnace bath, dissolving other oxides on its way. The slag is periodically removed from the furnace through a slag opening. The slag removed from the smelting furnace is often granulated and utilized in the building materials industry. Reverberatory-furnace matte consists of 80 to 90 per cent sulphides of copper and iron and 10-20 per cent of oxides of other metals by weight. The consumption of standard fuel amounts to 11-25 per cent of the weight of the charge. The degree of recovery of copper and noble metals of the matte in reverberatory furnaces lies at 96-99.5 per cent. The sulphurous gas discharged from a reverberatory furnace contains only 1.5 per cent  $\text{SO}_2$ .

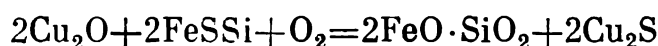
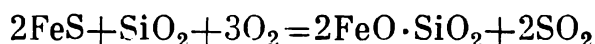
Smelting a concentrate in an electric furnace is a variant of the reverberatory-furnace process. This modification has a number of advantages, but is not widely used due to the high cost of the electric power consumed.

Shaft furnaces (see Part I, Fig. 73) are employed as a rule for producing matte from a lump ore, i.e. an ore which is directly subjected to smelting. In this case preroasting is not practiced, since during such roasting the lumps of the ore disintegrate and, besides this, the sulphur contained in the ore serves as a source of heat for the process in the shaft furnace and preliminary burning of the sulphur is not desirable.

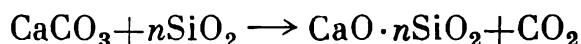
When a copper ore is smelted in a shaft furnace fluxes and coke are added to the ore, in the same fashion as in the case of a reverberatory furnace. Air enters the shaft furnace at the bottom through the tuyeres. The highest intensity of burning of the pyrite and the coke in a shaft furnace for smelting copper ores is in the tuyeres zone, where the temperature reaches 1400-1500 °C. The hot gases rising up through the furnace pass through the charge. At the level of the throat the gas temperature is 400-550 °C. The charge, which settles down through the shaft countercurrent to the hot gases, is gradually heated and the pyrites, chalcopyrite and other higher sulphides dissociate. The sulphur vapours produced are carried away by the gas and are oxidized to SO<sub>2</sub> and SO<sub>3</sub>. The carbon of the coke is oxidized by oxygen and sulphur dioxide



The most important reactions occurring during the smelting operation are:



The fluxes form low-melting calcium silicates:

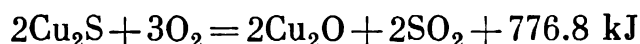


The molten mixture of sulphides and silicates flows to the bottom and is removed from the smelting furnace for separation into two layers in a settler, which is called the front hearth. The ore, flux and coke loaded into a shaft furnace should be in lumps from 20 to 150 mm in size. Conversion of the copper into the matte in blast furnaces is significantly lower than in reverberatory furnaces and only amounts to 78-85 per cent.

*Reprocessing the matte into blister copper*, independent of the method used for making the matte, is carried out in one and the same way: the molten matte (Cu<sub>2</sub>S · nFeS) is poured into a converter and air is blown through it. During the first stage of the blowing operation iron is oxidized and is transformed into slag by quartz added to the converter; this takes place by the following exothermic reactions:



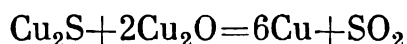
Copper sulphide may partially be oxidized to copper oxide (I):



However, as a result of interaction with FeS, the copper oxide (I) is reconverted to the sulphide

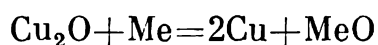


It follows that during the first stage of the blowing operation only oxidation of FeS can occur. Formation of copper oxide (I) becomes possible only when all the iron has been oxidized. After the slag has been tapped off, a molten body consisting mainly of  $\text{Cu}_2\text{S}$  remains in the converter; it is known as white matte. The content of copper in it is about 80 per cent. As more air is blown through the material  $\text{Cu}_2\text{S}$  is oxidized to copper oxide (I) and the latter reacts with  $\text{Cu}_2\text{S}$  to produce copper



The copper produced in a converter contains 98.4-99.4% Cu and is known as blister copper. Copper-smelting converters have the form of a horizontal cylinder with tuyeres, through which air is introduced, located along the side. The converter temperature should be approximately 1250 °C.

*Refining of blister, or black, copper* is the last operation. The copper contains impurities—Fe, Ni, S, Zn, As, Sb, Bi, Sn, Pb, Se, Te, Au, and Ag. It also contains dissolved gases. The copper used in engineering should contain not less than 99 per cent Cu and the blister copper must therefore be refined (purified). Two methods of refining copper are in use—fire refining (in reverberatory furnaces) and electrolytic refining. In fire refining the blister copper is melted in a reverberatory furnace at a temperature of 1300 °C. The oxygen contained in the hot gases passing over the molten copper partially oxidizes it to  $\text{Cu}_2\text{O}$ . The latter reacts with the impurities (Me) and oxidizes them by the reaction

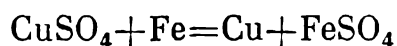


The metal oxides formed rise to the surface of the molten copper in the form of a slag which can easily be separated from it: some of the impurities are removed with the gases. Phosphoric alloys are also used for deoxidizing the copper. Fire refining is employed when the copper contains only small amounts of the noble metals and their recovery is uneconomical, the copper produced is not very pure (99.5-99.7 per cent Cu).

*Electrolytic refining* is a better method for removing impurities from copper. Anodes weighing up to 350 kg are cast from the blister copper; they are used in cells containing an aqueous  $\text{CuSO}_4$  solution to which sulphuric acid has been added as the electrolyte (30-40 g/l  $\text{CuSO}_4$  and 200 g/l  $\text{H}_2\text{SO}_4$ ). The cathodes are thin sheets of pure electrolytic copper.

When direct current is passed through the bath the anode gradually dissolves and pure copper is deposited on the cathode. The refined copper contains 99.9-99.95 per cent Cu. The sludge produced during electrolysis is processed and the noble metals, selenium, and sometimes tellurium, are recovered from it.

*The hydrometallurgical process* for treating copper ores is based on leaching to transfer the copper to solution. Leaching can be carried out using sulphuric acid, with copper sulphate being formed, or using ammonia or a solution of ammonium carbonate. In the latter case complex ammonium salts are produced in the solution. The copper is won from the solutions by electrolysis or by displacing it with iron (cementation), for example,



Hydrometallurgical processes are used mainly for treating poor, oxidized ores and their importance in modern copper metallurgy is not very great.

### 1. Electrochemical Processes

Electrochemical processes are processes which are effected by direct electric current. Electrolysis of aqueous solutions and of molten masses has extensive commercial applications. In a number of cases electrochemical production methods have many advantages over usual chemical methods: the technological process is simpler, the raw materials and the energy are utilized more fully, several valuable products are obtained simultaneously, the products possess high purity, unattainable by usual chemical manufacturing methods.

Owing to these advantages, electrochemical methods are used in a large number of diverse processes, the most important of which are the manufacture of chlorine, alkalies, hydrogen, oxygen, inorganic oxidizing agents (permanganates, persulphates, hydrogen peroxide and others); the winning and refining of metals (aluminium, magnesium, zinc, sodium, copper and others); and decorative and protective coating of metals.

Electrochemical methods also have drawbacks, the most important of which is large consumption of electric power; the cost of the electric power comprises the major fraction of the cost of the product. Rational utilization of electric energy is a question of primary importance in this case.

Indices which describe rational utilization of electric power in electrolysis are the current efficiency and the energy efficiency.

*The current efficiency*,  $\eta$ , is the ratio of the amount of the substance ( $G_a$ ) actually produced in the electrolysis process by expending a certain amount of electricity to the amount of the substance ( $G_t$ ) which should have been produced according to Faraday's laws. The current efficiency is usually expressed in per cent

$$\eta = \frac{G_a}{G_t} \cdot 100 \quad (7.1)$$

The theoretical amount of the substance can be calculated from the equation

$$G_t = \frac{I\tau \cdot E}{1000} \quad (7.2)$$

where  $I$  is the electric current, A;  $\tau$  the duration of electrolysis, hrs; and  $E$  the electrochemical equivalent—the amount of the substance

liberated at the electrode per A-hr (1.323 for chlorine, 1.492 for sodium hydroxide, 0.0376 for hydrogen).

**Example.** In a 24 hr period in a bath for electrolysis of common salt with the current at 15 500 A, 4200 l of electrolytic solution with a 125 g/l content of NaOH was produced. Find the current efficiency.

**Solution.** According to (7.2), theoretically, the following amount of sodium hydroxide should have been obtained

$$G_t = \frac{15\,500 \cdot 24 \cdot 1.492}{1000} = 555 \text{ kg}$$

Actually the amount produced was

$$G_a = \frac{125 \cdot 4200}{1000} = 525 \text{ kg}$$

It follows that the current efficiency was

$$\eta = \frac{G_a}{G_t} \cdot 100 = \frac{525}{555} \cdot 100 = 94.6\%$$

In commercial processes the current efficiency is always below 100%, as a result of side chemical or electrochemical processes. To increase the current efficiency measures should be taken which retard these processes.

*The energy efficiency* is defined as the ratio of the theoretical amount of energy  $W_t$  required for producing a unit of the product to the actual consumption  $W_a$ . Expressed in per cent it is equal to

$$\mu = \frac{W_t}{W_a} \cdot 100 \quad (7.3)$$

The theoretical energy consumption, kWh, per unit product obtained, is given by

$$W_t = \frac{v_t I \tau}{G_t} \quad (7.4)$$

where  $v_t$  is the theoretical decomposition voltage, V.

The actual amount of energy consumed depends on the voltage applied to the electrolytic cell,  $v_a$ ,

$$W_a = \frac{v_a I \tau}{G_a} \cdot 100 \quad (7.5)$$

Consequently, if  $W_t$  from equation (7.4) and  $W_a$  from equation (7.5) are substituted into equation (7.3) we obtain

$$\mu = \frac{v_t}{v_a} \eta \% \quad (7.6)$$

It follows from equation (7.6) that the energy efficiency grows with an increase in current efficiency and with a decrease in the voltage applied to the bath cell.

Theoretically electrolysis should begin when the voltage applied to the cell exceeds, even by an infinitely small amount, the theoretical decomposition voltage, equal to the difference between the equilibrium potentials of the anode reaction,  $\varphi_{ae}$ , and the cathode reaction,  $\varphi_{ce}$ , in the given conditions, i.e.

$$v_t = \varphi_{ae} - \varphi_{ce} \quad (7.7)$$

The equilibrium electrode potentials can be calculated using the Nernst equation

$$\varphi = \varphi^0 \pm \frac{RT}{zF} \ln C \quad (7.8)$$

where  $\varphi^0$  is the standard electrode potential, V;  $R$  the universal gas constant, l·atm/g-mole·deg;  $T$  the temperature, °K;  $z$  the charge of the ions;  $F$  the Faraday number, 96 000 coul; and  $C$  the concentration, g-eq/l. Actually a voltage  $v_a$  is applied to the cell which is the sum of the theoretical voltage  $v_t$  and the voltage for overcoming concentration polarization,  $\varphi_{conc}$ , anode  $\varphi_a$  and cathode  $\varphi_c$  overvoltages\* and also ohmic resistance of the electrolyte, electrodes, contacts and the diaphragm (if there is one),  $\sum IR$ :

$$v_a = (\varphi_{ae} - \varphi_{ce}) + \varphi_{conc} + (\varphi_a - \varphi_c) + \sum IR \quad (7.9)$$

where  $R$  is the electrical resistance (ohms).

Equation (7.9) is the so-called voltage balance. In industrial electrolysis, in spite of measures taken to minimize it, the actual voltage  $v_a$  is considerably above the theoretical value. The voltage balance for a cell with an iron cathode and graphite anodes used for electrolysis of sodium-chloride solutions is given below.

Anode potential $\varphi_{ae}$ , V	1.320
Cathode potential $\varphi_{ce}$ , V	0.820
Chlorine-liberation overvoltage $v_a$ , V	0.192
Hydrogen-liberation overvoltage $\varphi_c$ , V	0.210
Ohmic losses $\sum IR$ , V	1.051

At a current efficiency value of 96% the energy efficiency is

$$\mu = \frac{1.320 + 0.820}{3.593} \cdot 96 = 57.2 \%$$

The degree of useful consumption of energy is even lower in electrolysis of melts. Thus, in making aluminium from  $\text{Al}_2\text{O}_3$  dis-

---

\* Overvoltage is the name given to the difference between the potential at which an ion is liberated at an electrode in given conditions and the equilibrium potential for these conditions. Overvoltage is a result of a low rate of one intermediate stage, or several of them, of the discharge of some ions at an electrode. It follows that the larger this difference is, i.e. the larger the overvoltage, the higher will the electrode potential actually be.



solved in cryolite ( $\text{Na}_3\text{AlF}_6$ ) the voltage applied to the cell  $v_a = 4.4$  V, whereas the decomposition voltage  $v_t = 1.1$  V. At a current efficiency of approximately 85% the energy efficiency will be

$$\mu = \frac{1.1}{4.4} \cdot 85 = 20.3\%$$

In this case the energy losses are mainly due to high ohmic resistances of the electrolyte, current busses, electrical contacts, etc.

## 2. Electrolysis of Aqueous Solutions.

### The Manufacture of Chlorine and Sodium Hydroxide

Commercial electrolysis of aqueous solutions can be carried out either with deposition of metals at the cathode or without deposition of metals. Of all the electrochemical processes in use for decomposition of aqueous solutions without deposition of metals, the electrolysis of aqueous solutions of sodium chloride is carried out on the largest scale.

**Electrolysis of aqueous sodium-chloride solutions.** Electrolysis of aqueous solutions of sodium chloride produces chlorine, hydrogen and sodium hydroxide (caustic soda).

*Chlorine* at atmospheric pressure and normal temperatures is a yellow-green gas with an acrid odour. At standard conditions its density is 3.21 kg/cu m. The boiling point of chlorine at atmospheric pressure is  $-33.6^\circ\text{C}$ , and its freezing point is  $-102^\circ\text{C}$ . Chlorine is soluble in water and in organic solvents and it is extremely active chemically.

The principal user of chlorine is the chemical industry—for manufacturing various organic chlorinated derivatives, intermediates for making plastics, synthetic rubber, chemical fibres, solvents, insecticides, etc. At present more than 60% of the chlorine produced in the world is utilized in organic-synthesis processes. Besides this, chlorine is employed in making hydrochloric acid, calcium hypochlorite, chlorates and other products. Considerable amounts of chlorine are used in metallurgy for chlorination of polymetallic ores, winning gold from its ores and also in petroleum chemistry, in agriculture, in medicine and as an antiseptic for purifying drinking water and waste waters, in manufacturing fire-works and in a number of other branches of the economy.

Due to the increase in the uses of chlorine, which is a result mainly of the developments in the field of organic synthesis, world chlorine production now exceeds 20 million tons per annum.

*Sodium hydroxide*, or *caustic soda*, is an opaque crystalline substance, very soluble in water, with a melting point of  $328^\circ\text{C}$  at atmospheric pressure. Both solid sodium hydroxide and its aqueous solutions are produced commercially. Sodium hydroxide is employed

in the pulp-and-paper, synthetic fibre, petroleum processing, organic synthesis, soap-manufacturing, paint and varnish, and many other industries.

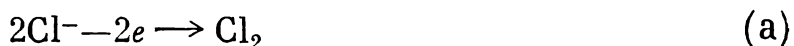
*Hydrogen* is a gas; the boiling point of hydrogen at atmospheric pressure is  $-252.8^{\circ}\text{C}$ . Hydrogen is employed in the synthesis of such highly important organic and inorganic products as ammonia, methanol and other alcohols, in hydrogenation of fats and solid and liquid fuels, in purifying petroleum products, etc.

*The raw materials* for manufacturing chlorine and alkalies are sodium-chloride brines obtained by dissolving rock salt or naturally occurring brines. The salt solution, irrespective of its origin, contains salts of calcium and magnesium, and before it is delivered to the electrolysis section of the plant these salts must be removed. Such purification is necessary to prevent formation of low-solubility calcium and magnesium hydroxides during electrolysis, which disrupts the normal course of the process.

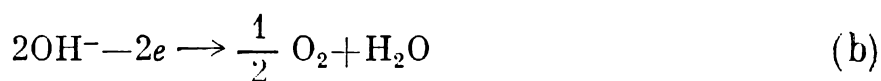
Soda and milk-of-lime solutions are used to purify the brine (see p. 107). Along with chemical purification, suspended solids are removed from the solutions by thickening and filtering operations.

Electrolysis of common-salt solutions is carried out in baths with a solid iron cathode and with diaphragms and in baths with a liquid mercury cathode. Industrial electrolyzers employed in a modern large scale chlorine plant should possess high production capacity, be of simple design, compact, and also reliable and stable in operation.

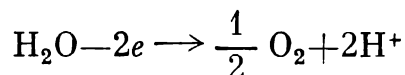
*By electrolysis of sodium-chloride solutions in cells with an iron cathode and a graphite anode* sodium hydroxide, chlorine and hydrogen can be produced in one and the same apparatus (electrolyzer). When direct electric current is passed through an aqueous solution of sodium chloride the substances liberated can be chlorine:



oxygen



or



The normal electrode potential of discharge of  $\text{OH}^-$  ions is  $+0.41 \text{ V}$ , and the normal electrode potential of discharge of chlorine ions is  $+1.36 \text{ V}$ . In a neutral saturated solution of sodium chloride the hydroxyl-ion concentration is approximately  $1 \cdot 10^{-7} \text{ g-eq/l}$ . At  $25^{\circ}\text{C}$  the equilibrium discharge potential of the hydroxyl ions will be

$$\varphi_{\text{ae}} = \varphi^0 - \frac{RT}{zF} \ln C = 0.41 - \frac{0.082 \cdot 298 \cdot 2.3}{1.96 \cdot 000} \log 10^{-7} = 0.82 \text{ V}$$

The equilibrium discharge potential of chlorine ions at a NaCl concentration of 4.6 g-eq/l is

$$\varphi_{ae} = \varphi^0 - \frac{RT}{zF} \ln C = 1.36 - \frac{0.082 \cdot 298 \cdot 2.3}{1.96 \ 000} \log 4.6 = 1.32 \text{ V}$$

Corresponding to this, at an anode with low overvoltage, oxygen should be liberated first. However, at graphite anodes the oxygen overvoltage may be higher than the chlorine overvoltage and, therefore, mainly  $\text{Cl}^-$  ions will give up their charge, with chlorine being liberated according to reaction (a). Chlorine liberation is promoted by increasing the NaCl concentration of the solution, which lowers the equilibrium potential. This is one of the reasons why concentrated sodium-chloride solutions, containing 310-315 g/l NaCl, are used for electrolysis.

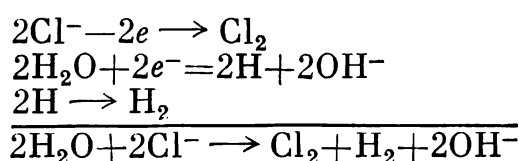
The molecules of water are discharged at the cathode in an alkaline solution by the reaction



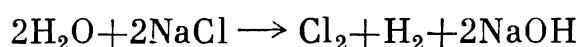
The hydrogen atoms recombine and are liberated in the molecular-hydrogen form:



The sodium ions in aqueous solutions cannot be discharged at a solid cathode because of their high discharge potential compared to that of hydrogen. The result is that the hydroxyl ions in the solution together with the sodium ions form a sodium-hydroxide solution. The process of NaCl decomposition can be described by the following equations:

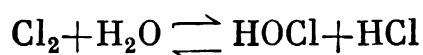


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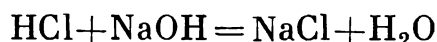
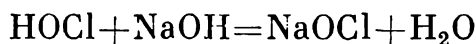
i.e. chlorine is produced at the anode and hydrogen and sodium hydroxide at the cathode.

During electrolysis, along with the principal processes there may be other, side, reactions, one of which is represented by equation (b). Also, chlorine liberated at the anode partially dissolves in the electrolyte and it hydrolyzes by the reaction:



In case of diffusion of the alkali (the  $\text{OH}^-$  ions) to the anode or of mechanical mixing of the cathode and anode products hypochloric and hydrochloric acids will be neutralized by the alkali to form

sodium hypochlorite and sodium chloride:



The  $\text{ClO}^-$  ions are easily oxidized to  $\text{ClO}_3^-$  at the anode. It follows that as a result of side reactions electrolysis will produce sodium hypochlorite, chloride, and chlorate and this will lead to a drop in the current efficiency and in the energy efficiency. Moreover, an alkaline medium favours liberation of oxygen and this also reduces the electrolysis indexes.

To retard these side reactions, conditions should be established which prevent mixing of the cathode and anode products. These

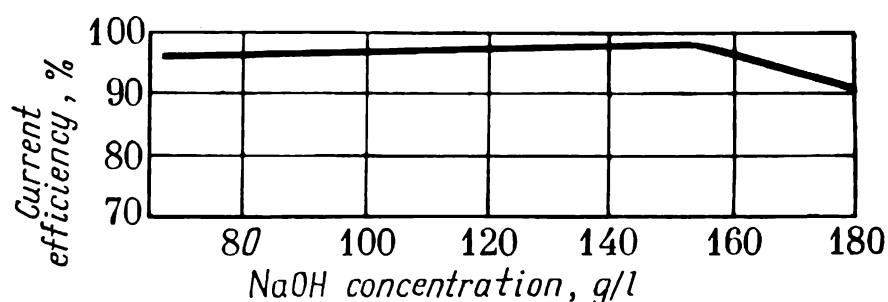


Fig. 55. Current efficiency vs sodium-hydroxide concentration of the catholyte

conditions are separation of cathode and anode zones with a diaphragm and filtering of the electrolyte through the diaphragm counter-current to the flow of the  $\text{OH}^-$  ions to the anode. Such diaphragms are called filtration diaphragms and are usually made of asbestos.

By raising the temperature of electrolysis and the  $\text{NaCl}$  concentration of the electrolyte, which lower the solubility of chlorine, and also by reducing the  $\text{NaOH}$  concentration of the catholyte the probability of side processes occurring is decreased. The current efficiency of electrolysis of a sodium-chloride solution at a given moment can be determined approximately using the equation

$$\eta = 1 - \frac{0.82}{1 + 0.512 \frac{C_1}{C_2}} \quad (7.10)$$

where  $C_1$  and  $C_2$  are the concentrations of  $\text{NaCl}$  and  $\text{NaOH}$  in the solution, respectively.

Equation (7.10) shows that the current efficiency decreases with an increase in the  $\text{NaOH}$  concentration and a drop in the sodium-chloride concentration. The effect of the concentration of alkali in the catholyte on the current efficiency is shown in Fig. 55, from which it follows that raising the  $\text{NaOH}$  concentration above 155 g/l results in a sharp decrease in the current efficiency.

Raising the temperature increases not only the current efficiency, but also the conductivity of the electrolyte and, as a result, it lowers

the voltage applied to the cell. It follows that raising the temperature decreases electric-power consumption and therefore electrolysis of sodium-chloride solutions is usually carried out at 70-80 °C.

*Cells with a filtering diaphragm* are extensively employed commercially. The principle of operation of a cell of this type is illustrated by Fig. 56. The cell has a perforated iron cathode and graphite anode. There is a filtering diaphragm made of asbestos sheet in intimate contact with the cathode. The sodium-chloride solution is fed to the anode department, and it filters through the diaphragm to the cathode.

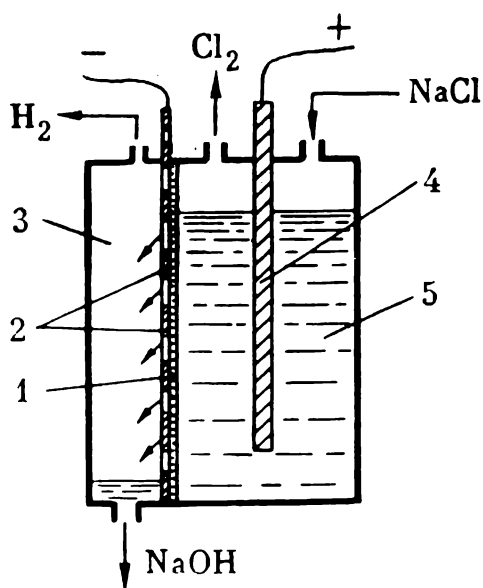


Fig. 56. Schematic diagram of a cell with a filtering diaphragm:

1—diaphragm; 2—steel cathode; 3—cathode department; 4—anode; 5—anode department

ode; the alkali passes through the openings in the cathode into the cathode department and is discharged from the cell.

Decomposition of the salt is not complete and constant concentrations of alkali and the undecomposed salt are established in the cell. The electrolyte solution flowing out of the cell contains 110-120 g NaOH and 170-180 g NaCl per litre.

Industrial electrolyzers must possess high capacity, and this is achieved by increasing their load. The use of cathodes with a very large surface area makes it possible to design compact electrolyzers with loads of up to 50 000 A. The diaphragm in this case is deposited on the cathode surface by suction, using a vacuum, from a suspension of asbestos fibres in a salt-alkali solution.

A cell with a deposited diaphragm is shown in Fig. 57. This cell consists of three basic parts—a concrete base, steel cathode and concrete top. The base has the form of a rectangular trough; the lower ends of the graphite anodes and a copper rod through which current is fed are supported on it by means of cast lead. The anodes are graphite plates. Recently, more efficient ruthenium oxide, deposited on

the cathode. The rate of electrolyte filtration is described by the so-called diaphragm penetrability  $v$  (cm<sup>3</sup>/hr) and it depends on the area of the diaphragm  $F$  (cm<sup>2</sup>), the hydrostatic pressure of the electrolyte  $h$  (cm w.c.), the thickness of the diaphragm  $b$  (cm) and the viscosity of the electrolyte  $\mu$  (cP)

$$v = \frac{Fh}{b\mu}k \quad (7.11)$$

where  $k$  is a penetration factor, which depends on the porosity of the diaphragm.

When direct electric current is passed through the cell, chlorine is liberated at the anode, and hydrogen and the alkali at the cathode.

titanium, anodes have come into use. The cathode is a steel frame with a number of flat pockets made of steel mesh mounted in it. The disposition of the pockets and their width are selected such, that when the cathode is put into place in the base of the bath, the pockets are located exactly between the anodes. The top of the cell

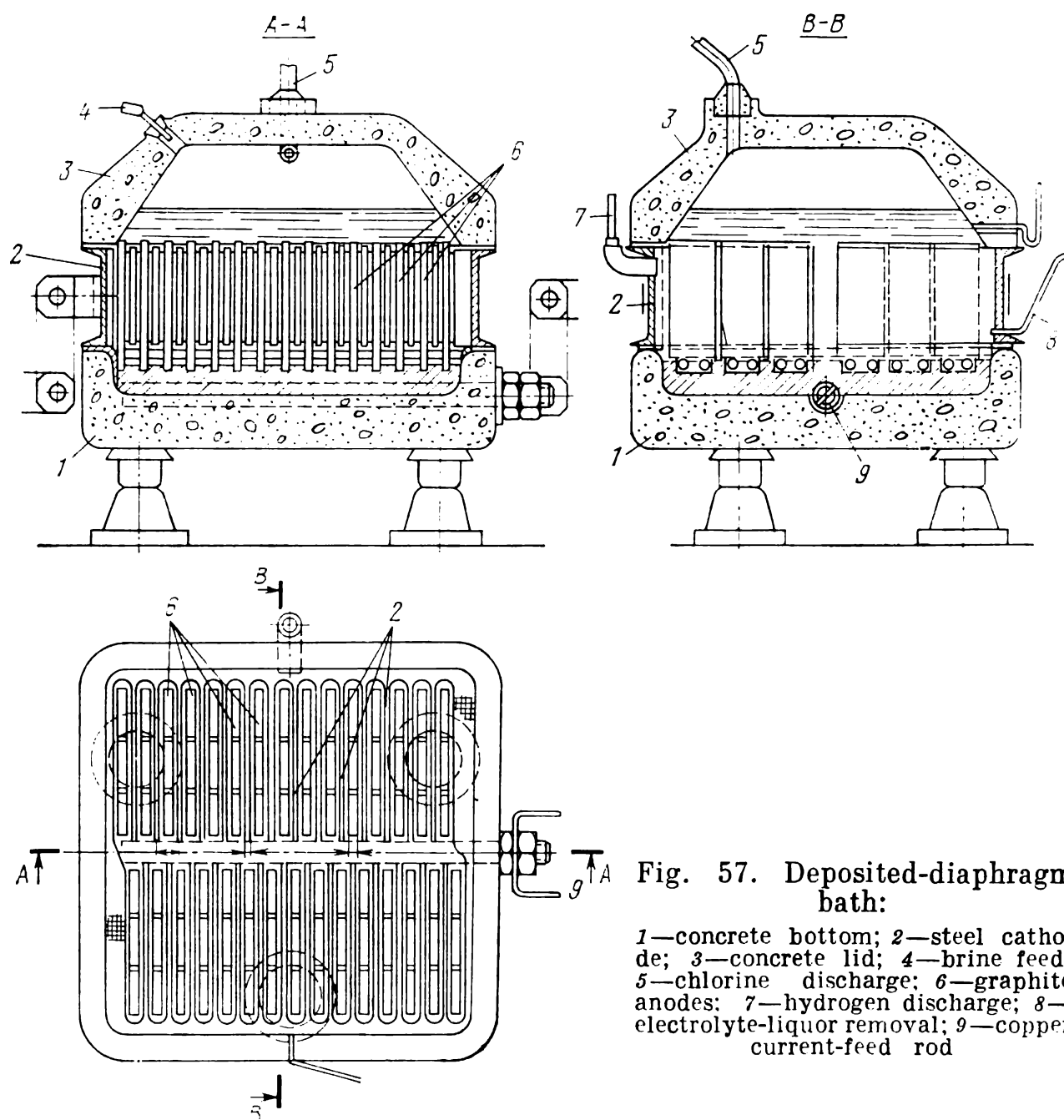


Fig. 57. Deposited-diaphragm bath:

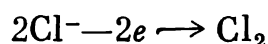
1—concrete bottom; 2—steel cathode; 3—concrete lid; 4—brine feed; 5—chlorine discharge; 6—graphite anodes; 7—hydrogen discharge; 8—electrolyte-liquor removal; 9—copper current-feed rod

has openings for feeding brine to it and withdrawing chlorine. The bath is heat insulated to decrease energy consumption due to heat losses to the atmosphere.

Cells with deposited diaphragms operate at 94-97 °C. The cell load is 10 000 A, the voltage 3.75 V, the current efficiency is 96% and energy efficiency may be as high as 60%.

By electrolysis of nitrogen-chloride solutions in *baths with a mercury cathode and graphite anode* the products are obtained with higher

concentrations than in diaphragm cells. When direct electric current is passed through a NaCl solution the  $\text{Cl}^-$  ions give up their charge at the graphite anode and gaseous chlorine is produced:



At a mercury cathode liberation of hydrogen takes place with a large overvoltage. Whereas the potential for hydrogen liberation at an iron cathode from a neutral solution is 0.415 V, the potential

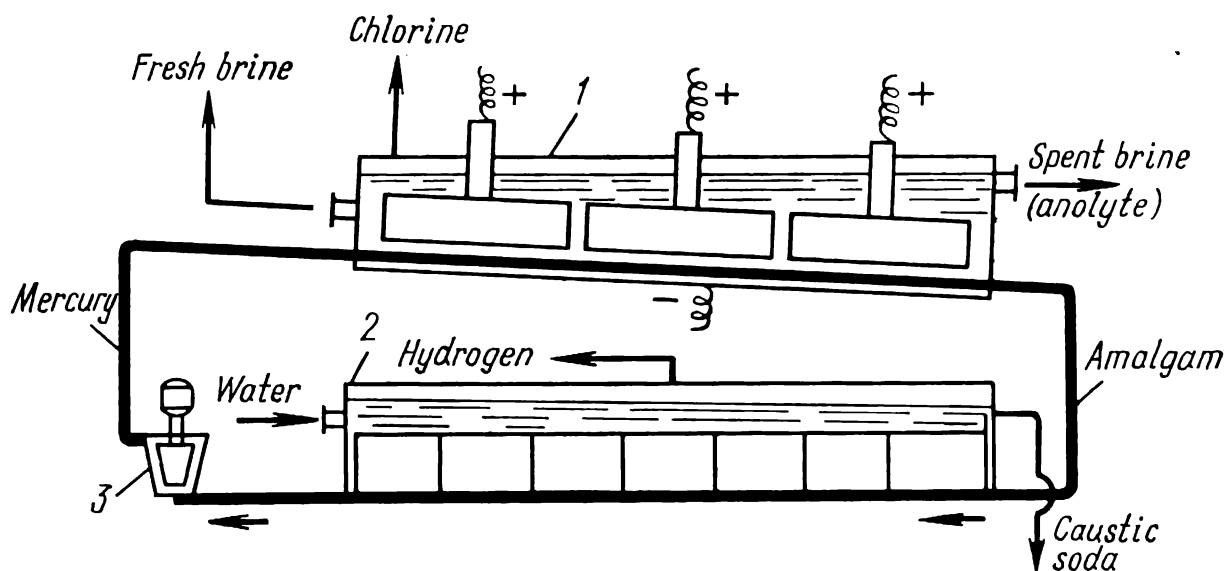
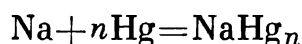
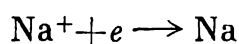


Fig. 58. Mercury-cathode bath:

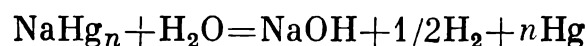
1—electrolyser; 2—decomposer; 3—pump

at a mercury cathode is 1.7-1.85 V. Moreover, there is a large depolarization effect when sodium is liberated on mercury, resulting from the formation of the sodium amalgam  $\text{NaHg}_n$ , which dissolves in an excess of mercury. As a result, the potential at which sodium gives up its charge to a mercury cathode is below the equilibrium voltage, i.e. it is 1.2 V, as compared with the equilibrium potential of 2.71 V. Consequently, the following processes occur at a mercury cathode:



and practically no hydrogen is liberated.

The sodium amalgam is decomposed with water in a special decomposer unit by the reaction:



Electrolysis in a cell with a mercury cathode is usually carried out at a voltage of 4.3-4.4 V.

A cell with a mercury cathode, whose schematic diagram is given in Fig. 58, consists of two parts: an electrolyzer proper and a decomposer. The electrolyzer and decomposer may be separated and only

connected by a pipe, or they may be contained in one common shell. The electrolyzer is a long box of rectangular cross section, with a lid at the top in which the graphite anodes are fastened. The cathode current buss ends at the slightly inclined cell floor, along which a thin layer of mercury flows. In this way the cell bottom serves as the cathode. A concentrated sodium-chloride solution (310-315 g/l) is fed to the electrolyzer, and the salt concentration drops to 260-270 g/l during the electrolysis processes. The weak brine is removed from the cell, chlorine is desorbed under vacuum with compressed air blown through the brine, after which the brine is again brought up to the saturation point with salt, purified (not shown in the diagram) and returned for electrolysis. The chlorine formed is removed through the cell lid.

As the mercury flows along the cell bottom, in the course of electrolysis a sodium amalgam is formed which dissolves in the mercury and is removed from the cell to the decomposer unit. There are various designs of decomposers—both horizontal and vertical ones. Horizontal decomposers consist of a rectangular trough with a lid. Water is fed to the decomposer and the products formed—hydrogen and caustic soda—are continuously removed. The bottom of the decomposer is slightly inclined and, as a result, the mercury flows down it, is discharged and delivered by a lift of some kind to the electrolyzer cell.

Cells with mercury cathodes occupy large floor space due to the horizontal position of the cathode. There are cells in which the cathodes are in the form of vertical amalgamated discs. These cells are compact, but their design and operation are more complicated.

A comparison of the basic operation indexes of the two types of cells (Table 8) shows that due to the high voltage applied to cells with a mercury cathode, energy consumption in such cells is higher than in diaphragm cells. Moreover, operation of cells with a mercury

TABLE 8  
Operating Indexes of Electrolyzer Cells

Index	Electrolyzer cell			
	Deposited diaphragm		Mercury cathode	
	BTK-25	BTK-50	P-101	P-300
Load, A	25 000	50 000	150 000	300 000
Voltage, V	3.45	3.7	4.6	4.7
Current efficiency, %	96	96	95	95
Energy consumption per ton Cl, kWh	2720	2920	—	—
Chlorine production capacity, tons per day	0.765	1.53	4.5	9.04



cathode is more complicated than that of diaphragm cells; capital outlay is larger and working conditions at plants equipped with mercury cells are worse than at plants with diaphragm cells.

The possibility of producing concentrated liquors which do not contain salt in mercury cells is an important advantage. Because of this, in all cases where high-purity caustic soda is required (for instance, in manufacturing viscose fibres) baths with mercury cathodes are preferred. As a result of the increase in the demand for high-purity caustic soda electrolysis in baths with mercury cathodes has come to be most extensively used.

In electrolysis plants the direct electric current is fed to cells connected in series. The number of cells in a series depends on the voltage of the current rectifier. Usually 60 to 70 cells are connected in series, and the direct current is supplied by a 240 to 280 V source.

The caustic-soda solution produced by electrolysis is concentrated in evaporator units. Diaphragm-cell caustic soda contains up to 130-140 g/l NaOH and 170-180 g/l NaCl. The solubility of the common salt decreases with an increase in the NaOH-concentration. For instance, in a brine containing 50% (769 g/l) NaOH at 20 °C solubility of NaCl is 13.9 g/l. As a result when the electrolyzer liquor produced in diaphragm cells is evaporated, crystalline sodium chloride is precipitated as the concentration of the solution grows, and it is recycled to electrolysis. Industrially, following the evaporation and melting operations, the alkali contains 92-94% NaOH and 2-3% NaCl.

The hydrogen is delivered to the consumer without being processed in any way or it is discharged to the atmosphere. The chlorine produced is saturated with water vapour. The chlorine is dried in two stages. First it is cooled to 20-30 °C in coolers and the moisture is partially condensed, after which the chlorine, for final drying, is passed through a packed tower to which vitriol oil is fed at the top. The dry chlorine obtained is pumped to the consumer plant through steel tubes (dry chlorine does not corrode metals) by fans or rotary compressors.

At many plants the chlorine is liquefied. Chlorine can be liquefied by one of three methods: (1) by compressing it to 10-12 atm at room temperature; (2) by cooling it to approximately -50 °C at atmospheric pressure; and (3) by raising the pressure to 3-6 atm and cooling to a temperature from -5 to -25 °C. The liquid chlorine is put into steel cylinders, drums or cisterns with capacities of up to 50 tons, for delivery to the consumer.

### 3. The Manufacture of Hydrochloric Acid

Hydrochloric acid is a solution of hydrogen chloride in water. Hydrogen chloride is a colourless gas; hydrogen chloride has a melting point of -114.2 °C and a boiling point of -85 °C. Hydrogen

chloride is highly soluble in water, the solubility depending very strongly on the temperature. At a gas pressure of 760 mmHg one litre of water at 0 °C dissolves 525.2 l HCl (the solution contains 46.15% by weight HCl); at 18 °C 451.2 l HCl is dissolved (the solution contains 42.34% by weight HCl). Hydrogen chloride forms an azeotropic mixture with water which contains 20.24% HCl and boils at 110 °C at a pressure of 760 mmHg.

Hydrogen chloride is used in significant amounts for hydrogen-chlorination of organic compounds.

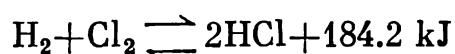
Hydrochloric acid is used in making inorganic salts of zinc, barium, etc., in non-ferrous metallurgy, electroforming, for production of chloroprene,  $\text{CH}_2\text{CClCHCH}_2$ , vinyl chloride,  $\text{CH}_2\text{CHCl}$ , for making aniline dyes, for starch hydrolysis (in manufacturing alcohol) and in a number of other industrial processes. There are two standard concentrations of commercial hydrochloric acid: 27.5 and 31% HCl. The production of hydrochloric acid consists of two stages: production of hydrogen chloride and absorption of the hydrogen chloride with water. The various processes for manufacturing hydrochloric acid differ in the method used for obtaining the hydrogen chloride.

*The sulphate process for manufacturing hydrogen chloride* is one of the oldest in the chemical industry. It is based on the reaction of sodium chloride with concentrated sulphuric acid described by the equation



The reaction is carried out at 500-550 °C in a muffle-type furnace; it produces solid sodium sulphate and a gas which contains 30 to 40% hydrogen chloride. At present, this method has been almost completely replaced by more efficient direct synthesis of HCl.

*Synthesis of hydrogen chloride* is carried out using chlorine and hydrogen obtained by electrolysis of aqueous salt solutions. Hydrogen burns in chlorine exothermically by the reaction



The rate constant,  $k$ , of this reaction grows with the temperature in accordance with the Arrhenius equation.

The equilibrium constant of the reaction of hydrogen chloride formation is given by

$$K_p = \frac{p_{\text{HCl}}^2}{p_{\text{H}_2} p_{\text{Cl}_2}} \quad (7.12)$$

or

$$K_p = 4x_e^2 / (1 - x_e)^2 \quad (7.13)$$

where  $p$  denotes the partial pressure of a component at equilibrium.

The dependence of the equilibrium constant on the temperature is expressed by

$$\log K_p = \frac{9586}{T} - 0.44 \log T + 2.16 \quad (7.14)$$

Using equations (7.13) and (7.14) the dependence of  $x_e$  on the temperature was calculated:

$t$ °C	$x_e$
17	$2.51 \cdot 10^{-17}$
727	$1.34 \cdot 10^{-5}$
1727	$0.41 \cdot 10^{-2}$
2227	$1.30 \cdot 10^{-2}$

This shows that decomposition of HCl into the elements becomes significantly large only at very high temperatures—above 1500 °C. Industrially the reaction is carried out by tranquil burning of hydrogen in chlorine at 2300-2400 °C. There is a 5 to 10% excess of hydrogen in the reaction mixture to provide fuller utilization of the chlorine.

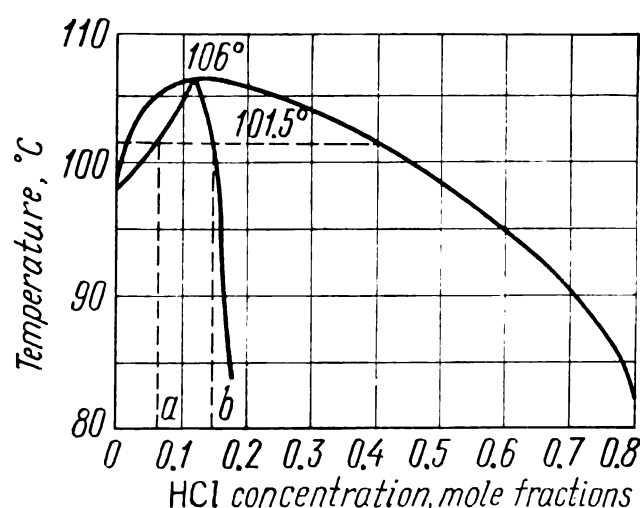


Fig. 59. Phase diagram for the HCl-H<sub>2</sub>O system

The reaction between chlorine and hydrogen is carried out in furnaces (see Part I, Fig. 26) operating at close to plug flow conditions. The gas leaving the furnace contains 80 to 90% HCl, and hydrochloric acid with a concentration of over 31% can be made from it. Large amounts of hydrogen chloride are also obtained as a by-product at organic-synthesis plants.

*Absorption of hydrogen chloride with water* leads to formation of hydrates and liberation of heat.

If the heat of solution is not removed during the absorption process the temperature of the acid will rise and it will not be possible to obtain acid with concentrations above that of the azeotropic mixture. For producing acid with higher concentrations intensive removal of the heat of solution was practised, which involved the use of large-size absorption apparatus. In the USSR A. M. Gasparian developed a method for absorbing hydrogen chloride without removing the heat of HCl-solution to the ambient air (adiabatic absorption). The temperature of the acid rises adiabatically and can be calculated using (3.89) (see Part I). The heat of solution of the HCl is consumed for evaporating water.

Fig. 59 is a phase diagram of the H<sub>2</sub>O-HCl system, which shows how the boiling point of hydrochloric acid depends on the concentration at a pressure of 700 mmHg. The maximum boiling point

under these conditions corresponds to a 20% HCl-content in the solution (0.13 mole fraction) and is approximately 106 °C. If the temperature is lowered to 101.5 °C, for instance, during boiling of the solution, then the acid concentration can either decrease (point *a*) or increase (point *b*). Whether the concentration grows or drops depends on the composition of the gas phase. If the amount of hydrogen chloride in the gas phase exceeds the amount which corresponds to the azeotropic mixture, the concentration of the acid will grow; but if there is less hydrogen chloride, the acid concentration will drop. High-concentration gas is fed to the absorption unit from the furnaces, and, therefore, adiabatic absorption produces high-strength acid.

The continuous countercurrent process is carried out in an absorption tower which requires only four theoretical trays to achieve a 27.5% acid concentration and 5 theoretical trays for a 31% concentration. Commercially, packed towers are frequently used. They are made of materials which are not corroded by hydrochloric acid: ceramic ware, quartz, plastics (faolite, PVC plastic).

#### 4. Electrolysis of Fused Electrolytes. The Manufacture of Aluminium

Only such substances can be produced by electrolysis of aqueous solutions whose potential of discharge at the cathode lies above the potential for hydrogen discharge. Such electronegative metals as lithium, potassium, calcium, sodium, magnesium, aluminium, and others cannot be won from aqueous solutions on solid cathodes and they are produced commercially exclusively by electrolysis of molten salts, oxides, hydroxides, or their mixtures. The metals are almost always produced in a molten state in the process. The molten electrolytes are governed, on the whole, by the same laws of electrochemistry which apply to aqueous solutions, although there are some specific features characteristic for electrolysis of melts.

*Electrolysis of fused electrolytes* is carried out at high temperatures produced by the heat liberated when direct electric current flows through an electrolyte. It follows that the electric power is used for decomposing the substance, for melting the electrolyte and for making up for heat losses.

The lower temperature limit for an electrolysis process is the temperature at which the electrolyte or the metal solidifies. In order to carry out electrolysis at relatively low temperatures complex mixtures which form low-melting eutectics are used as electrolytes. Practically, the temperatures used vary within a wide interval, from 310 to 1400 °C.

*Aluminium* is a light metal with a density of 2.7 g/cm<sup>3</sup> at 20 °C, a melting point of 659 °C and a boiling point of approximately

2500 °C. It is an excellent conductor of both electricity and heat. In an oxidizing medium, for instance in air, a dense oxide film is formed on the surface of aluminium, and this film makes it corrosion-resistant. Aluminium is stable in nitric and organic acids.

Aluminium is used in alloys with other metals to increase its mechanical strength and improve casting properties. The most extensively used alloys are those of aluminium with copper, magnesium and manganese called duraluminums and also alloys with silicon—Silumins.

Due to the combination of low weight, high strength, and high heat and electrical conductivity aluminium and its alloys are most important materials in making aeroplanes, automobiles, transportation devices, internal combustion engines, in electrical engineering, etc. Aluminium and its alloys are used in the chemical industry for making tubes, tanks and various apparatus.

*The raw material* from which aluminium is manufactured is alumina ( $\text{Al}_2\text{O}_3$ ) obtained from various minerals: bauxites, nepheline, alunite, etc. The most important is bauxite, which contains  $\text{Al}(\text{OH})_3$ , or  $\text{AlOOH}$ , together with oxides of iron, silica and other impurities.

In processing the raw material into alumina for further conversion into aluminium a product of high purity must be obtained since impurities can seriously disrupt the electrolysis process. Production of alumina is a very complex process. It combines chemical conversion with a number of physical operations: fine grinding of the raw material, heating and cooling, settling, filtering, etc. Essentially the process of manufacturing alumina consists in separating the aluminium hydroxide from the other minerals.

The aluminium hydroxide is converted to sodium aluminate,  $\text{NaAlO}_2$ , by reacting it with soda (sintering) or sodium hydroxide (leaching); the aluminate is soluble in water and this makes it possible to separate it from the oxides of iron, which are insoluble in these conditions. However, silica,  $\text{SiO}_2$ , is also partially dissolved, in the form of  $\text{Na}_2\text{SiO}_3$ . It is deposited from the solution as  $\text{CaO} \times \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  or  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$  and removed by filtering. The  $\text{Al}(\text{OH})_3$  is deposited from the purified aluminate solution by various methods, for example by carbonation—bubbling carbon dioxide through the aluminate solution; it combines with the  $\text{Na}^+$  ions to form soda. The aluminium hydroxide separated from the solution is calcined and a product containing up to 99%  $\text{Al}_2\text{O}_3$  is obtained. The yield of aluminium oxide, the end product, does not exceed 60%.

*Aluminium is manufactured* from alumina dissolved in cryolite ( $\text{Na}_3\text{AlF}_6$ ). Cryolite is a convenient solvent because  $\text{Al}_2\text{O}_3$  is soluble in it, it contains no ions more positive than aluminium, it is a good conductor of electricity, but allows the heat necessary for melting the electrolyte to be developed, and it forms alloys with the alumina

whose melting points are much lower than that of pure alumina (2050 °C). The melting diagram of the  $\text{Al}_2\text{O}_3$ - $\text{Na}_3\text{AlF}_6$  system composed by Fedotiev and Ilyinsky is given in Fig. 60. It shows that if 15% alumina is dissolved in cryolite the melting point of the electrolyte drops to 938 °C. Actually, electrolysis is carried out with about 10%  $\text{Al}_2\text{O}_3$  in the electrolyte at a temperature of 950-1000 °C.

Roughly the process consists of liberation of molten aluminium at the cathode and combustion of the carbon anode by the oxygen discharged on it. If the temperature of the electrolysis process is 1000 °C, aluminium has a density of 2.35 g/cm<sup>3</sup>, whereas the density of cryolite containing 10% alumina is 2.03 g/cm<sup>3</sup>. The heavier aluminium collects at the bottom of the bath and is periodically removed. Inasmuch as the electrodes are gradually consumed during the process the anodes must be of special design to provide continuous action.

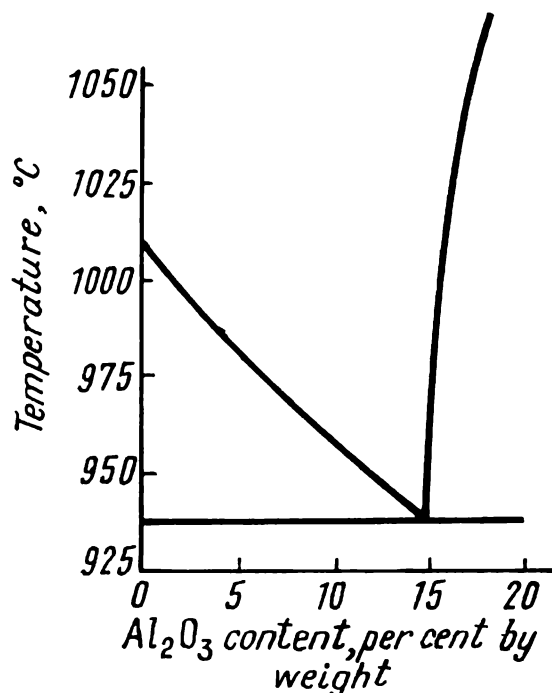


Fig. 60. Phase diagram for the  $\text{Al}_2\text{O}_3$ - $\text{Na}_3\text{AlF}_6$  system

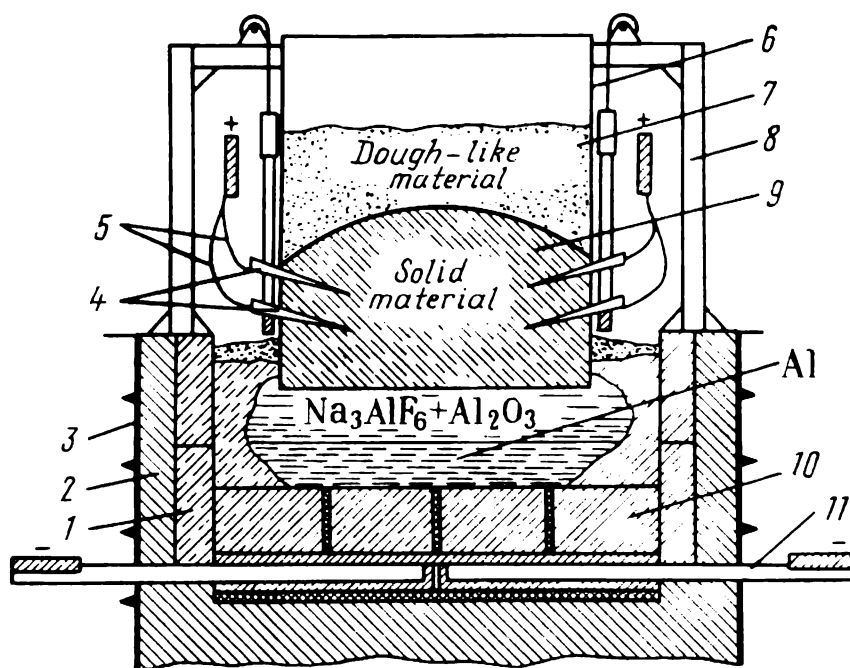


Fig. 61. Electrolyzer with self-baking anodes:

1—graphite slabs; 2—refractory brick; 3—shell; 4—steel pins; 5—current busses; 6—aluminium shell; 7—anode; 8—frame; 9—anode material; 10—graphite blocks; 11—cathode-current feeder

*Cells with self-baking anodes* operate without stops for changing the anodes. A cell of this type is shown in Fig. 61. The cell shell is lined

with firebrick and graphite slabs. The cell bottom serves as the cathode; it is made of graphite blocks to which steel current-busses are connected. A so-called self-baking anode is suspended above the bath on a frame. The anode consists of an aluminium shell which contains the anode material (a mixture of anthracite, coke, coke tar, and pitch). At the top the anode material is in a plastic state, and at the bottom, where it is subjected to high temperatures, it is solid. As the anode burns out the anode mechanism on the frame is lowered, and the material within it sinters and is transformed into a carbon block. Aluminium shell is periodically added at the top, and fresh electrode material is loaded into it. The current is fed to the anode through a current-buss and through steel spikes hammered into the anode material. As the anode burns the lower row of spikes is removed and they are hammered into the material and form a new row at the top. In this way self-firing electrodes provide continuous action.

Electrolysis is carried out at a potential of 4.2-4.5 V and a load of 80 000-150 000 A with a current efficiency of 88-90%. Energy consumption amounts to 16 100-16 200 kWh per ton. Aluminium produced from alumina contains impurities, mainly iron and silicon. For obtaining pure aluminium the technical-grade aluminium is refined.

### 1. General

Fuels are naturally occurring or manufactured combustible organic substances which serve as a source of heat or as raw materials for the chemical industries. The very rapid growth of the organic-synthesis industry—the manufacture of plastics, synthetic fibres, synthetic rubber, varnishes, dyes, solvents, etc.—has created a demand for huge amounts of the hydrocarbon raw materials which are obtained by chemical processing of various fuels.

A few years ago the principal source of raw materials for the synthesis of organic products was coal, from which benzene, toluene, xylene, phenol, naphthalene, anthracene, hydrogen, methane, ethylene, and other products were obtained in the process of carbonization. Petroleum in the earth always contains dissolved gases which are separated when the petroleum is brought to the surface. These casing-head gases consist of methane, ethane, propane, butane and other hydrocarbons. Each ton of petroleum produced yields on the average 30 to 50 cu m of the gas, which is a very valuable raw material of the chemical industry. Another source of hydrocarbon raw materials is the gases produced in processing petroleum: during cracking, pyrolysis, and reforming. These gases contain both saturated hydrocarbons (methane, ethane, propane, butane) and olefinic hydrocarbons (ethylene, propylene and others). Along with gas phase hydrocarbons, some aromatic hydrocarbons—benzene, toluene, xylenes, and their mixtures may also be formed when petroleum is processed.

One of the basic raw materials of the chemical industry is natural gas, which contains up to 98 per cent methane. Natural gas is utilized for making organic products and ammonia. Wood and wood-waste are the initial materials from which cellulose, ethyl alcohol, acetic acid, furfural and a number of other products are manufactured. Combustible gases, raw material for making lubricants, motor fuels, hydrocarbons, etc. are produced from shale and peat.

All fuels can be classified according to their phase state as solid, liquid or gaseous and according to their origin as natural or synthetic.

The group of natural fuels includes solid fuels—coal, wood, shale, and peat; liquid fuels—petroleum; and gaseous fuels—natural gas and casing-head gas.



The group of synthetic fuels, which are mainly produced by processing natural fuels, includes such solid fuels as coke, low-temperature semicoke, charcoal; such liquid fuels as petrol, kerosene, ligroin, fuel oil and others; and such gaseous fuels as producer gas, coke-oven gas, petroleum-refinery gases, etc.

*The composition and properties of solid fuels.* Solid fuels contain combustible organic materials and an incombustible, or mineral part (ballast).

*The organic portion of a fuel* consists mainly of carbon, hydrogen and oxygen. Besides these the organic portion may also include such elements as nitrogen and sulphur. The composition of various fuels is presented in Table 9. The ratio of the various elements in a fuel determines its properties.

TABLE 9

## Composition of Fuels

Fuel	Organic part, %			Mois- ture, %	Ash, %	Sul- phur, %	Vola- tile mat- ter, %	Heat of combus- tion, kJ/kg
	C	H	O + N					
Wood	44.0	6.0	50.0	30-40	0.4	0.0	> 70	18 850
Peat	59.0	6.0	35.0	25	4.5	0.4	70	23 900
Brown coal	70.0	5.5	24.5	≤ 50	4.0	2-3	45-55	25 550
Coal	82.0	5.0	13.0	3-8	6.0	2-6	8-50	33 920
Anthracite	95.0	2.0	3.0	1.3	6.0	1-2	8	33 500
Shales	75.0	10.0	15.0		50.0			33 920

*The incombustible part of a fuel* consists of moisture and minerals. The amount of moisture in the fuels depends not only on the type of fuel, but also on the method used for mining and storing it. Average moisture contents in fuels are listed in Table 9.

*The mineral part of a fuel* consists of carbonates, silicates, phosphates, sulphates, sulphides of iron, calcium, magnesium, aluminium, potassium, sodium, etc. When a fuel is burned or gasified the minerals form a residue, the ash; many of them decompose and form oxides. In pyrolysis the ash is a part of the solid fuel residue. The ash contents of various fuels are given in Table 9. Sulphur is an important impurity which affects the quality of a fuel and the products obtained by processing it. It is contained in fuels in the form of sulphides (sulphide sulphur), sulphates (sulphate sulphur), and organic compounds (organic sulphur). During combustion or gasification of a fuel the sulphide sulphur and organic sulphur are oxidized and produce sulphur dioxide, whereas sulphate sulphur usually remains in the ash. In dry distillation of a fuel the sulphur is distributed among

the various products, but the largest amount is left in the solid remainder. Average amounts of sulphur in various fuels are listed in Table 9.

*The volatile matter* refers to the gaseous and liquid products (at high temperatures, the latter are in the form of vapours) which are produced by heating a fuel in the absence of air. The moisture contained in the fuel is also separated from it together with the volatiles. The yield of volatile matter (the loss in the weight of a fuel when it is heated in the absence of air at 850 °C for seven minutes with the moisture content subtracted) can be used to estimate whether it is rational to subject the fuel to chemical processing to produce liquid and gaseous products. The yield of volatiles of various fuels is shown in Table 9.

**The heat of combustion of a fuel** is the amount of heat which is liberated by burning unit weight or unit volume of the fuel. The heat of combustion is an index describing the properties of a fuel as a source of energy, it is expressed in joules; its value depends on the composition of the fuel and on its moisture content. The values of the heat of combustion of various fuels are listed in Table 9.

**The composition and properties of petroleum and petroleum products.** Petroleum consists mainly of carbon (83-87 per cent) and hydrogen (12-14 per cent), of which the hydrocarbons of the complex mixture are essentially composed. Besides hydrocarbons, petroleum also contains small amounts of non-hydrocarbons and mineral impurities.

*The hydrocarbon portion* consists of paraffin (alkane), naphthene (cyclane) and aromatic hydrocarbons. There are, as a rule, no unsaturated hydrocarbons (olefines) in petroleum, but they are present in the petroleum products. Gaseous paraffin hydrocarbons (from  $\text{CH}_4$  to  $\text{C}_4\text{H}_{10}$  inclusive) are present in the petroleum in the dissolved state. When the petroleum is brought from the depths of the earth to its surface and the petroleum pressure drops the gaseous hydrocarbons separate from it as the casing-head gas. The principal part of the liquid fraction of the petroleum and of the liquid fractions obtained when it is processed consists mostly of liquid paraffin hydrocarbons (from  $\text{C}_5\text{H}_{12}$  to  $\text{C}_{15}\text{H}_{32}$  inclusive). There are solid hydrocarbons (from  $\text{C}_{16}\text{H}_{34}$  and higher) dissolved in the petroleum and they can be separated from it. The naphthenic hydrocarbons present in the petroleum are mainly derivatives of cyclopentane and cyclohexane.

Aromatic hydrocarbons are found in petroleum in relatively small amounts, mainly in the form of benzene and its homologues—toluene and xylenes; some amounts are also formed in processing petroleum.

Depending on the predominant kind of hydrocarbons in a petroleum, it is classed as a paraffinic, naphthenic-paraffinic, naphthenic, paraffinic-naphthenic-aromatic or aromatic petroleum.

*The non-hydrocarbon part* of a petroleum consists of sulphur-, oxygen- and nitrogen compounds. The sulphur, present in petroleum in amounts from 0.1 to 7.0%, is in the form of mercaptan-, sulphide-, and disulphide-, fatty compounds. With respect to their sulphur content petroleums are classed as low-sulphur content petroleum (for example Caucasian petroleum) and high-sulphur content petroleum (petroleum from the Bashkir and Tartar fields). The oxygen-containing constituents of the petroleum are naphthenic acids, tars, and asphaltic compounds. The high-molecular tars and asphaltic compounds give the dark colour to the petroleum. They are chemically unstable and readily decompose to form coke when heated. The nitrogen compounds in petroleum are pyridine- and quinoline derivatives, and amines. The content of oxygen and nitrogen in petroleums is up to 1.5 and 2.2%, respectively.

*The mineral impurities in petroleum* are mechanical impurities, mineral salts, and ash. The mechanical impurities—particles of sand and clay—are entrained by the petroleum on its way to the earth's surface. Water is contained in petroleum in two forms: water which can be separated from petroleum by settling and water in stable emulsions, which can only be destroyed by special methods. The mineral salts, for instance calcium chloride and magnesium chloride, are dissolved in the water contained in the petroleum. The ash makes up only hundredths, or even thousandths, of a per cent of the petroleum weight, it contains sodium, calcium, magnesium, iron and other elements.

*The fractional composition of petroleum* is determined by subjecting it to fractional distillation, in which the petroleum is separated into fractions according to their boiling points. Depending on the boiling points of its principal fractions a petroleum is classified as light or heavy.

*The properties of a petroleum* depend on its composition. Petroleum is a viscous, opalescent liquid from light-yellow to dark-brown in colour. The density of most petroleums lies between 0.83 and 0.97 g/cm<sup>3</sup>, the hardening temperature is between +10 °C (petroleum with a high-paraffin content) and -20 °C (petroleum without paraffins), the heat of combustion is 39 800-44 000 kJ/kg.

**Methods for processing various fuels.** Extensive use is made of pyrogenetic methods for processing fuels; in these methods the physical and chemical transformations are brought about by high temperatures. Pyrogenetic processing of fuels can be accomplished in three basic ways: by gasification, hydrogenation and processing without available air, known as dry distillation or pyrolysis.

*Gasification of fuel* is a process for synthetic conversion of the organic part of a solid fuel to combustible gases by interaction with air, steam, oxygen or other gases. By means of gasification a low-value (in particular high ash-content) fuel is converted into a so-called

generator gas, which is an ashless fuel convenient for transportation and a raw material for the chemical industry. Depending on the gaseous agent employed for gasification of the fuel, i.e. the nature of the blast, and the technological regime of the process, air generator gas, water gas, steam-air gas, or steam-oxygen gas can be produced, which all differ in composition and properties. These gases can contain carbon monoxide, hydrogen, and methane as their combustible components. Gasification is carried out at temperatures between 900 and 1100 °C. The high temperatures are achieved at the expense of the heat of exothermic reactions between the gasifying agent and the fuel.

Gasification of fuels was formerly extensively employed in industry. However, at present, due to the increase in the production of natural and casing-head gases, which are widely employed as fuel and raw materials of the chemical industry, in a number of countries and at many industrial plants to a large extent generator gas has been replaced by natural gas.

*Hydrogenation* is a fuel processing method in which the fuel reacts chemically with hydrogen at high temperatures and in the presence of catalysts to yield products with a higher hydrogen content than that of the raw material. The high temperatures necessary for hydrogenation are achieved by heating the reactants with hot gases through the reactor walls and also as a result of exothermic reactions. Hydrogenation methods are used for processing both liquid and solid fuels.

*Dry distillation of a fuel* takes place when it is heated with no air available. Such heating may result in: (a) physical processes, for instance, separation of liquid fuels into fractions with different boiling points, etc., and (b) chemical processes—deep, destructive chemical transformations of the fuel components to yield a number of chemical products. The role and nature of the individual processes are not identical in the pyrolysis of different kinds of fuels. Most often the overall heat effect is negative (endothermic) and, consequently, heat must be supplied to the pyrolysis process from an external source. The reactors used are usually heated by means of hot combustion products which transfer heat to the fuel through the apparatus walls or by direct contact. Both solid and liquid fuels are subjected to dry distillation.

Dry distillation (pyrolysis) of solid fuels—coals, peat, wood, shales—is a complex process consisting of many parallel and consecutive reactions. In general, these reactions reduce to decomposition of the molecules of the fuel and polymerization, condensation, dealkylation, aromatization, etc. of the fission products.

The quality and the quantity of the products obtained by pyrogenetic processing of various fuels differ, and they depend primarily on the nature of the fuel being treated and secondly, for a fuel of

given kind, on the temperature conditions, on the duration of treatment at high temperatures, and on a number of other factors. Generation of solid, gaseous and vapour materials is characteristic of all pyrolysis processes.

## 2. Coal Carbonization (Coking)

Coking is a method employed for processing fuels, mainly coals, which consists of heating them in the absence of air to a temperature of 900-1050 °C. Under these conditions the fuel decomposes to form volatile products and a solid remainder—coke.

When the temperature of a coal is gradually raised its components undergo deep physical and chemical transformations: up to 250 °C water is evaporated and carbon monoxide and dioxide are liberated; at about 300 °C separation of coal-tar vapours and formation of pyrogenetic water begin; above 350 °C the coal becomes plastic; at 500-550 °C there is very active decomposition of the plastic body accompanied by liberation of primary products (gases and tar), and its solidification to form semicoke. When the temperature is raised to 700 °C there is further decomposition of the semicoke and separation of gaseous products from it; above 700 °C the principal process is hardening of the coke. The volatile products come into contact with the incandescent coke, the hot walls and roof of the coking chamber and undergo pyrolysis—they are converted into a complex mixture of vapours (predominantly compounds of the aromatic series) and a gas containing hydrogen, methane, etc. A large part of the sulphur in the original coal and all the mineral substances remain in the coke.

It follows from the above, that carbonization is a complex two-phase process in which heat transfer, diffusion and a large number of diverse chemical reactions participate. Coking of coal yields the following products: coke, coke-oven gas, coal tar, light oil, flushing water and ammonium salts (usually ammonium sulphate).

*The raw materials* for the coking process are coals which sinter well and produce high-strength, porous, metallurgical-grade coke. However, the charge used for making coke in industry does not consist of coking coals only; it also contains coals of other grades; for example a charge made up of Don-basin coals may contain 20 per cent gas coal; 40 per cent fat coal; 20 per cent coking coal; and 20 per cent lean coking coal. By mixing various grades of coal the raw-material basis of the coke industry is extended and high-quality coke can be produced with a high yield of coal tar, light oil, and coke-oven gas.

**Coking-process products and their use.** *Coke* is a solid, black, porous material. About 650-750 kg of coke are produced from a ton of the dry charge. It is employed mainly in metallurgy, but also for gasification, for manufacturing calcium carbide and electrodes, as a reactant and as a fuel in a number of branches of the chemical

industry. Since coke is most widely used in metallurgy this determines the properties required. The coke must possess high mechanical strength, or otherwise it will disintegrate in the metallurgical furnace under the pressure of the layer of charge above it and this raises the resistance to gas flow through the furnace, disrupts furnace operation, reduces its output, etc. The calorific value of the coke should be 31 400-33 500 kJ/kg. The coke should have good combustibility and high reactivity. The first of these indexes describes the rate at which the coke burns; the second characterizes the rate of reduction of carbon dioxide by the carbon of the coke. Since these are both heterogeneous processes, their rates depend not only on the composition of the coke, but also on its porosity, which determines the area of the interface between the reacting phases. The quality of coke also depends on its content of sulphur, ash, moisture and volatile substances.

During blast-furnace smelting the sulphur contained in the coke is transferred to the pig iron, which lowers its quality. A sulphur content of 1.2-1.7 per cent in coke is considered permissible. The coke ash is a ballast, and its content should not exceed 10-11 per cent. The volatiles in coke usually amount to about 1.0 per cent. Moisture in the coke reduces its calorific value, and the moisture content should not exceed five per cent.

*Coke-oven gas* is produced in amounts of 310-340 cu m per ton of dry coal. The composition and yield of the coke-oven gas depend mainly on the coking temperature. The coke-oven gas released from the coking chamber contains gaseous products, coal-tar vapours, light oil and ammonia liquor; this gas is known as the direct coke-oven gas. The gas obtained after the tar, light oil, water and ammonia are removed, is called return coke-oven gas (for its composition see page 177); it is employed as a raw material for chemical synthesis and also as an industrial fuel for heating coke ovens, steel-smelting furnaces, etc.

*The coal tar* is a viscous, dark-brown product with a characteristic odour; it consists of about 300 different substances. The most important components of the tar are the aromatic and heterocyclic compounds: benzene, toluene, xylene, phenol, cresol, naphthalene, anthracene, phenanthrene, pyridine, carbazole, coumarone, etc. The density of the tar is 1.17-1.20 g/cm<sup>3</sup>. The coal-tar yield is from three to four per cent of the weight of the coal in the dry charge. The tar composition depends mainly on the carbonization temperature, whereas the tar yield depends both on the temperature and on the nature of the coal raw materials. If the carbonization temperature is raised hydrocarbon pyrolysis is deeper and this reduces the yield of tar and increases the gas yield.

At present about 200 different products are recovered from the coal tar: these are mixtures and individual substances which serve as

raw materials for the synthesis of dyes, pharmaceuticals, insecticides and fungicides, plastics, synthetic fibres, etc.

*Light oil* is a mixture produced in the coking process which consists of carbon disulphide, benzene, toluene, xylene, coumarone, and other substances. The yield of light oil on the average comprises about 1.1 per cent of the weight of the coal taken. The light oil yield depends on the composition and properties of the coal raw material and on the temperature conditions of the process. Distillation of the light oil produces individual aromatic hydrocarbons and mixtures of hydrocarbons which are raw materials for chemical manufacturing process.

In the USSR the amount of coal mined for coking purposes exceeds 150 million tons per annum. With a coal tar yield of approximately 4% and a light oil yield averaging about 1%, coal tar produced is above 6 million tons and light oil—about 1.6 million tons per annum. Coal tar and light oil in such amounts in spite of the development of petroleum chemistry remain a most important source of aromatic hydrocarbons for the chemical industry.

*Flushing liquor* is a weak aqueous solution of ammonia and ammonium salts which also contains phenol, pyridine compounds and some other substances. The flushing liquor is processed to liberate the ammonia contained, which is utilized together with the ammonia of the coke-oven gas to produce ammonium sulphate and concentrated ammonia liquor.

**The design and operation of coke ovens.** Carbonization of coal is a high-temperature chemical process. The chemical reactions at first occur only in the solid phase. As the temperature rises gaseous and vapour products are formed and complex reactions occur within the solid and gas phases and between them as well. Because of this, it is difficult to employ the relationships for heterogeneous processes for determining the optimal conditions of the coking process. The most important of the factors on which the course of the coking process depends is the supply of heat, needed to heat the charge to the temperature of dry distillation and for carrying out the endothermic coking reaction. The limiting value of the temperature is determined by a number of factors; among them, a decrease in the yield of coal tar and light oil, changes in the composition of the carbonization products, destruction of the refractory materials employed in making the coke ovens, etc.

Coke ovens are indirectly heated furnaces—in them heat is transferred to the coal being carbonized from the heating gases through the furnace walls.

A coke oven, or a battery (Fig. 62), consists of 61-69 dens operated in parallel, which are in the form of long, narrow, rectangular in cross section channels made of refractory brick. Each den has removable front and back doors (not shown in the drawing), which are tightly

sealed when the charge is introduced into the chamber. The loading hatches in the roof of the chamber are opened for charging the coal, but closed during the coking process. The coal in the chamber is heated through the oven walls by combustion gases which flow through the heating partitions—the walls between the chambers. The hot combustion gases are produced by burning blast furnace gas, return coke-oven gas or, less often, producer gas. The excess heat of the

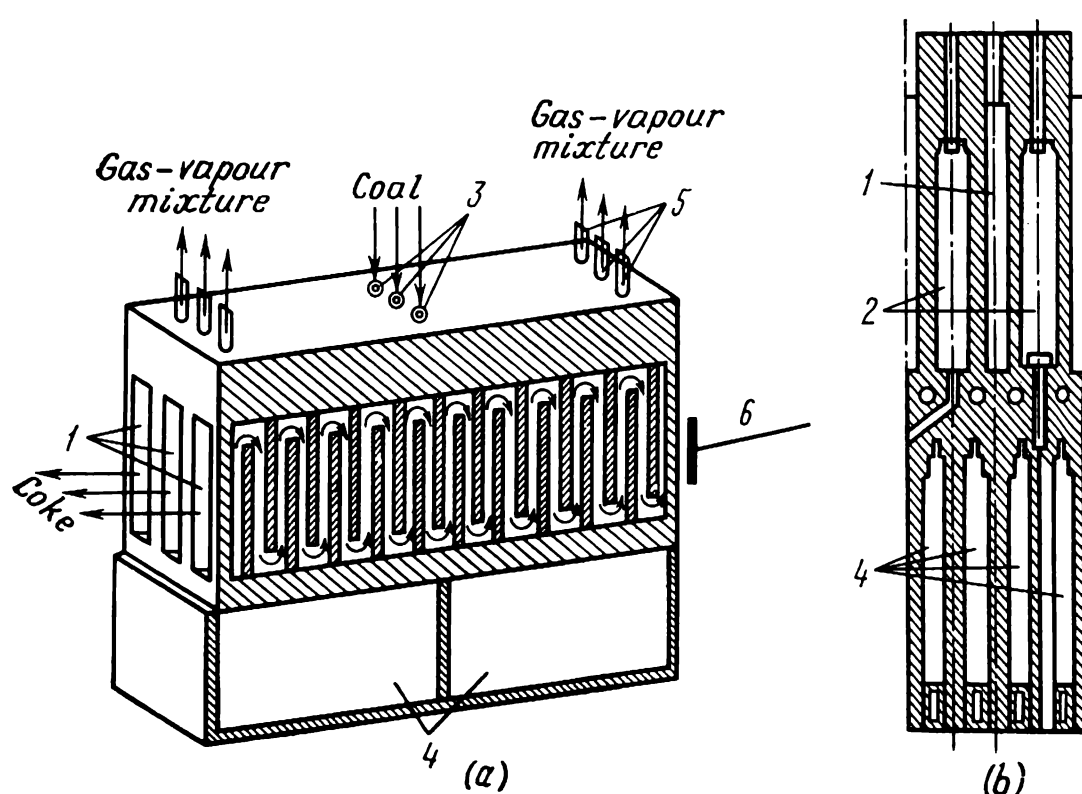


Fig. 62. Coke oven:

(a)—section through heating partition; (b)—cross-section drawing of the coke-oven chamber; 1—coking chamber; 2—heating partition; 3—charging holes; 4—regenerators; 5—risers; 6—coke pusher

combustion products at the exit from the heating partition-wall is utilized in regenerators to raise the temperature of the air and gaseous fuel employed for heating the coke ovens, and this increases the thermal efficiency of the oven.

During the operating period of a coke chamber the temperature of the coal charge must be raised gradually and uniformly. This depends on uniform distribution of the heating gases in the heating partition-wall and a proper selection of the den dimensions. Uniform distribution of the heating gases is achieved by dividing the heating-wall inner space with vertical partitions into a number of channels, known as verticals. The hot gases flow through the verticals, give up their excess heat to the chamber walls, and go on to the regenerator.

For steady-state conditions the amount of heat,  $Q$ , transferred in unit time in indirectly heated furnaces can be determined from the



equation

$$Q = k_t F \Delta t \quad (8.1)$$

where  $k_t$  is the heat transfer coefficient,  $\text{kJ/m}^2 \cdot \text{deg} \cdot \text{hr}$ ;  $F$  the heat transfer area,  $\text{m}^2$ ;  $\Delta t$  the difference in the temperatures of the heating gas in the heating flues,  $t_f$ , and the temperature of the coal charge,  $t_{ch}$ ,  $^{\circ}\text{C}$ . The heat transfer coefficient is given by

$$k_t = \frac{1}{\frac{1}{\alpha_1} + \frac{\delta_1}{\lambda_1} + \frac{\delta_2}{\lambda_2} + \frac{1}{\alpha_2}} \quad (8.2)$$

where  $\alpha_1$  and  $\alpha_2$  are the local heat-transfer coefficients from the heating gases to the furnace walls and from the walls to the coal charge, respectively,  $\text{kJ/m}^2 \cdot \text{deg} \cdot \text{hr}$ ;  $\delta_1$  the thickness of the wall,  $\text{m}$ ;  $\delta_2$  the half-thickness of the coal charge,  $\text{m}$ ;  $\lambda_1$ ,  $\lambda_2$  the heat conductivity of the wall and of the coal charge, respectively,  $\text{kJ/m}^2 \cdot \text{deg} \cdot \text{hr}$ .

To increase the heat-transfer coefficient, besides the usual techniques employed for raising  $\alpha_1$  and  $\alpha_2$ , the thickness of the wall and of the coal layer is minimized. Usually the thickness of the Dinas brick wall is about 0.1 m and the chamber width is 407–410 mm. The heat transfer area  $F$  depends on the size of the chamber.

The den length is limited by the strength of the walls under static loads, the difficulty of removing the pusher and the levelling rod (the device for levelling the top surface of the charge), the complexity of achieving uniform distribution of the gases in the heating flues. A chamber is approximately 14 m long. The height of the chamber must be such that it provides uniform heating over the chamber height. In this respect good results are obtained at a height of approximately 4.3 m.

A coke-oven den is a batch process reactor and, therefore, the temperature changes with time. Because of this the difference in the temperatures of the heating gases in the flues,  $t_f$ , and the coal charge,  $t_{ch}$ , ( $\Delta t = t_f - t_{ch}$ ) varies with time. Immediately after the coal has been charged into the chamber the  $\Delta t$ -value is large and therefore the amount of heat being transferred to the coal charge is high and the coal at the chamber walls begins to coke. However, the central layers of the charge remain at a low temperature. As the coal temperature rises, the amount of heat transferred in unit time drops, but the temperature across the chamber cross section gradually rises. Fig. 63a gives the isochronic (line of constant time) temperature distribution across the width of the charge in the chamber. If we could see the condition of the material in the chamber at a certain moment of the coking period, we would find (Fig. 63b) that near the walls a layer of coke has already been formed; further from the walls, where the temperature is lower, there is a layer of semicoke and near the chamber axis—a layer of coal in a plastic condition, and, finally,

at the chamber centre—coal which has undergone no change. As time passes the temperature distribution across the chamber width becomes more uniform, the coke layer widens out towards the chamber axis and eventually the coal charge becomes completely coked.

It follows that due to the change in the  $\Delta t$  value with time, the amount of heat transferred from the heating gas to the coal changes

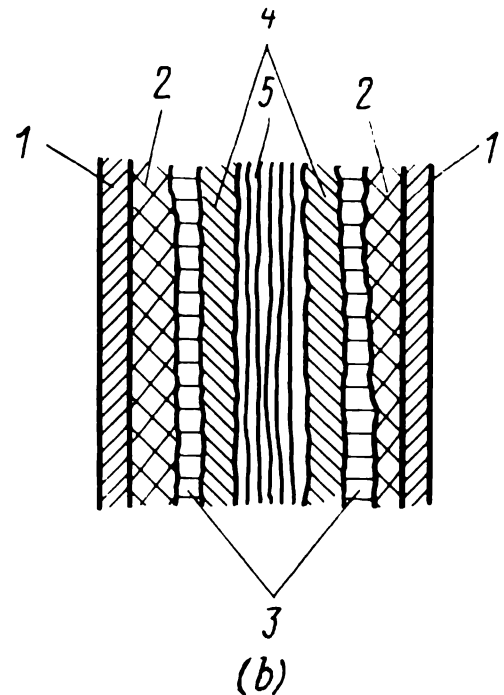
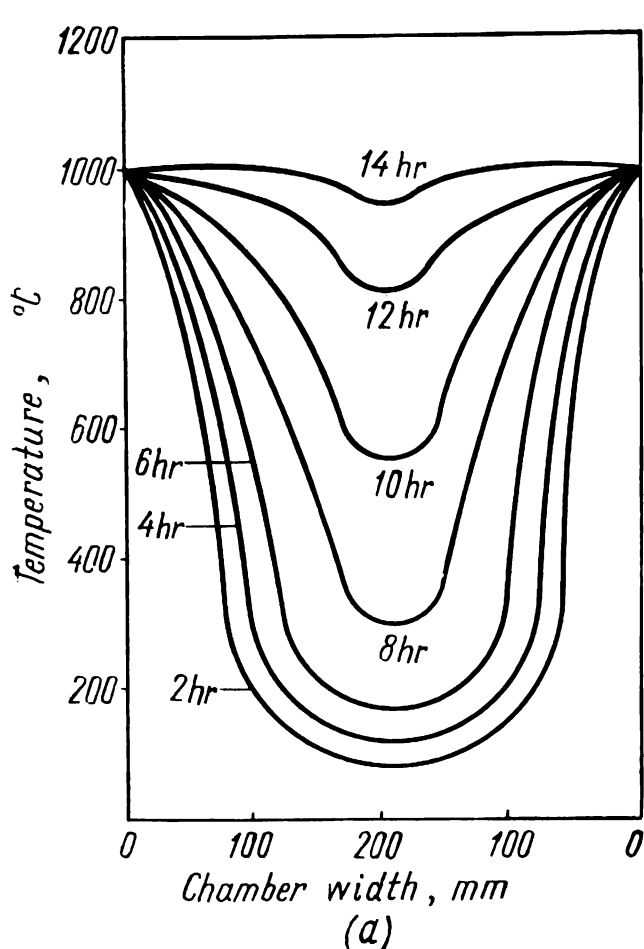


Fig. 63. Isochronic temperature distribution across the charge in the chamber (a) and a cross-sectional drawing of the charge (b):

1—chamber wall; 2—coke; 3—semicoke; 4—coal in a plastic state; 5—unchanged coal charge

markedly during the coking period and this must be taken into account in determining the duration of the coking process. If heat transfer for this case is considered as transfer through a flat plate, then the process, in a simplified form, is described by the equation

$$\tau = \frac{b^2}{4a} \cdot \frac{t_{ch}}{t_f} \quad (8.3)$$

where  $\tau$  is the coking period, hr;  $b$  the den width, m;  $a$  the thermal conductivity coefficient,  $\text{m}^2/\text{hr}$ .

Equation (8.3) can be used to determine the duration of the coking process, for example, for a den width  $b = 0.4$  m, conductivity coefficient  $a = 0.0024$   $\text{m}^2/\text{hr}$ , temperature of the coal charge  $t_{ch} = 1100$   $^{\circ}\text{C}$ , temperature in the flues  $t_f = 1400$   $^{\circ}\text{C}$ , the coking period will be

$$\tau = \frac{0.4^2 \cdot 1100}{4 \cdot 0.0024 \cdot 1400} = 13 \text{ hr}$$

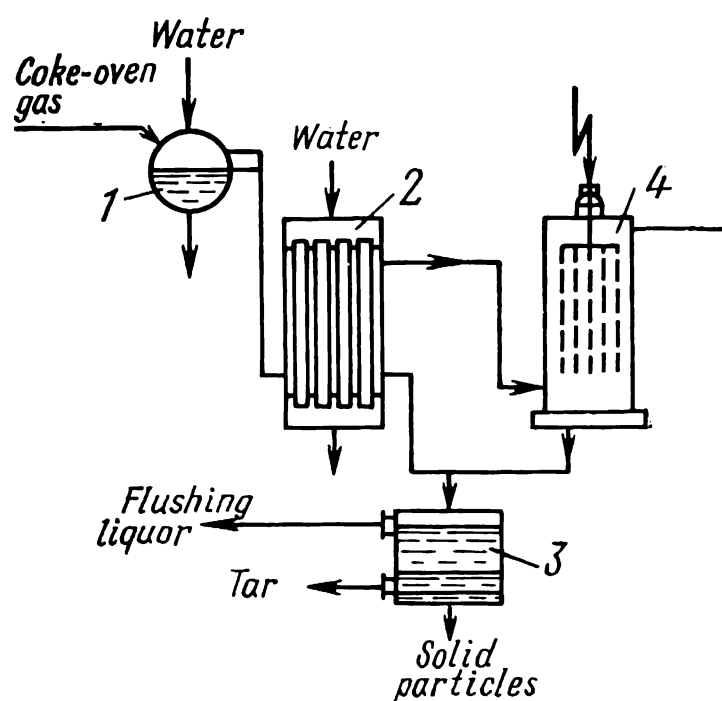


Fig. 64. Flow diagram of coke-oven gas processing:

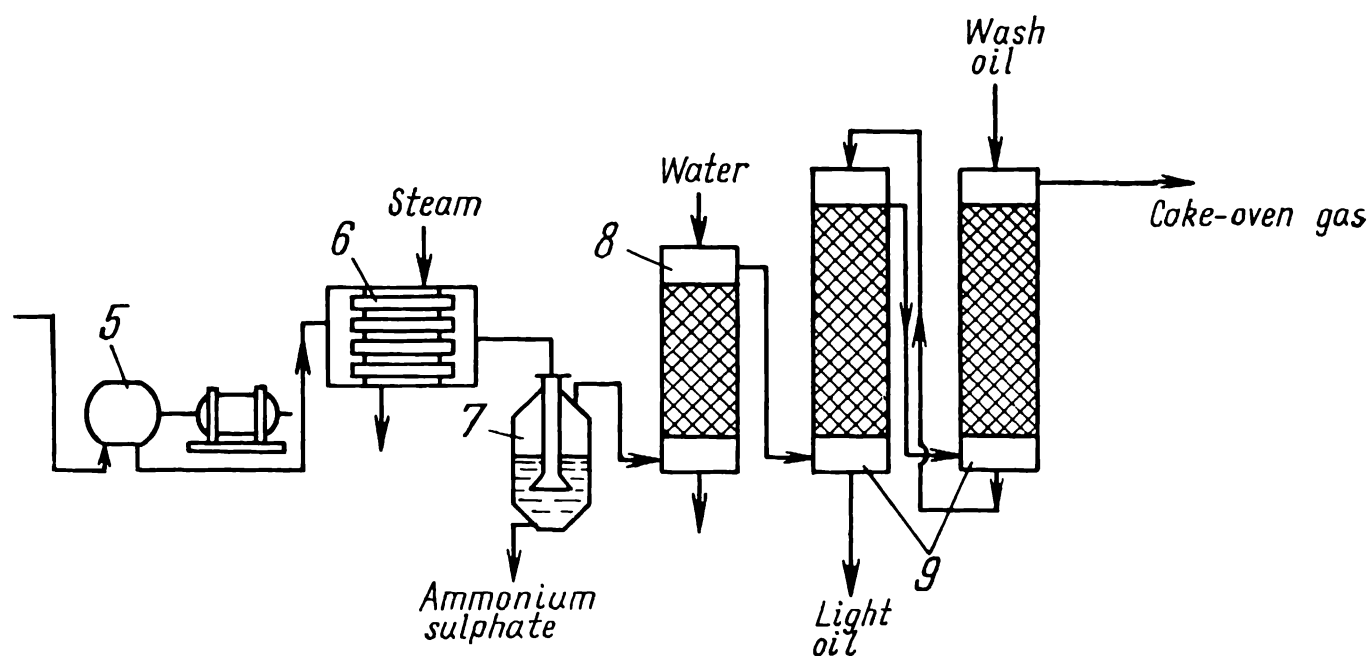
1—gas tank; 2—cooler; 3—reservoir;  
4—electrostatic precipitator; 5—exhaust-  
er; 6—heater; 7—saturator; 8—cooler;  
9—scrubbers

which is in good accord with the time necessary for completion of the process, as shown in Fig. 63a.

The mixture of vapours and gases formed in the coking process is continuously withdrawn from the chamber through a riser (see Fig. 64). When carbonization is completed, the front and back doors are removed by a specially designed mechanical device, the “coke cake” formed in the chamber is pushed out by a pusher machine and drops onto a quencher car, where it is cooled by drenching it with water; after it has dried the coke is sized.

It follows that coking in each chamber is a batch process. However, arranging a large number of chambers in a battery so that they operate in parallel provides continuous operation of the unit as a whole. The direct coke-oven gas leaving each den through risers continuously enters a common horizontal gas collector for all the ovens. All the chambers of the battery have these mechanisms in common: charging car, from which the coal is charged to the ovens, door-removing device, coke pusher, quencher car and quenching tower, in which water is poured onto the quencher car with the incandescent coke, and the coal tower-bunker, with the supply of coal charge for loading into the coking dens.

**Processing the carbonization products.** The first stage is separation of the components of the direct coke-oven gas. Tar and liquor are condensed and ammonia, light oil and hydrogen sulphide are separated out. Then the flushing liquor, coal tar and light oil are divided to obtain individual substances or mixtures. Separation of coking products is based on a number of typical procedures and unit operations of chemical technology: mass- and heat transfer by direct con-



tact between gases and liquids, heat transfer through a wall, condensation, physical absorption and chemisorption. Selective absorption, desorption, distillation, multiple rectification, fractional crystallization, separation of products by means of specific chemical reactions are also employed. In all these processes temperature is the principal factor; process conditions can be improved and process rates increased by close temperature control. By lowering the temperature of absorption the driving force of the process is raised [see Part I, Chapter 2, equation (2.71)], whereas desorption processes are accelerated by raising the temperature. To decrease the diffusion resistance at the phase interface and, correspondingly increase the mass-transfer coefficient, agitation of the media is intensified by increasing the rate of gas and liquid flow. This is especially effective in the case of countercurrent flow of gas and liquid in packed towers. To increase the liquid-gas interface towers with various types of packing, tray-type apparatus and spray towers are used for processing the coke-oven gas.

*The direct coke-oven gas* is a complex mixture of gaseous and vapour-form substances. Along with the hydrogen, methane, ethylene and other hydrocarbons, carbon monoxide, carbon dioxide and nitrogen, one cubic metre of the gas (at 0 °C and 760 mmHg) contains 80-130 g of coal tar, 8-13 g ammonia, 30-40 g benzene hydrocarbons, 6-25 g hydrogen sulphide and other sulphide compounds, 0.5-1.5 g hydrogen cyanide, 250-450 g water vapour and solid particles. At the exit from the coke ovens the gas has a temperature of about 700 °C.

**Processing of the direct coke-oven gas to separate it (Fig. 64)**

begins in the gas collector, into which cold flushing liquor is sprayed to cool the gas to approximately 80 °C, which results in partial condensation of the coal tar. Simultaneously, solid coal particles are removed from the gas. The gas must be cooled to 20-30 °C for condensation of the tar. Cooling can be carried out in coolers of various design—of the shell-and-tube, drip or direct-mixing type. In the flow diagram of Fig. 64 shell-and-tube coolers are used for condensing the water and coal-tar vapours. Lowering the gas temperature not only promotes the condensation of tar and water vapours, but also raises the solubility of ammonia in the water condensate, which results in partial absorption of the ammonia in the flushing liquor and increases the driving force of ammonia absorption due to the decrease in the equilibrium partial pressure of the ammonia vapour over the flushing liquor. Besides this, at low temperatures the volume of the gas flowing through the apparatus is reduced, which lowers power consumption for transporting the gas and reduces the size of the piping.

The tar plus flushing liquor from the coolers flow into a vat, where they separate into two layers of different densities. The coal tar is not all removed in the cooler, since part of it is present in the gas as a mist. The coal-tar mist is removed from the gas in electrostatic filters, which operate at a potential of 60 000 to 70 000 V.

The gas is drawn off from the ovens and transported through the apparatus by an exhaustor (turbo-blower). The ammonia remaining in the gas leaving the coolers is absorbed in a saturator with tower-grade sulphuric acid, which reacts with the ammonia to form crystalline ammonium sulphate. The pyridine compounds are removed from the gas in the saturator, along with the ammonia, pyridine sulphate being formed. The saturator is a bubble-type apparatus. The temperature is maintained at 60 °C by preheating the coke gas with steam in a shell-and-tube heater and by the heat released during the reaction. The  $(\text{NH}_4)_2\text{SO}_4$  crystals are removed from the saturator together with the mother liquor, are separated from the latter in centrifuges (not shown in Fig. 64) and are used as a nitrogenous fertilizer.

After the ammonia has been removed from it the gas is directed to the unit for light-oil recovery. The most commonly used method for recovering the light oil is absorption with solvent oils at 20-25 °C in scrubbers. Coal-tar oil (the distillation-fraction of coal tar which boils at 230-300 °C) or solar oil (petroleum-distillation fraction which boils at 300-350 °C) are used as absorbents. The gas entering the light-oil scrubber is preliminarily cooled with water in direct-mixing coolers, where naphthalene and small drops of sulphuric acid entrained in the saturator are also washed out of the gas.

Usually hydrogen sulphide and other sulphur compounds are removed from the coke gas after the light oil has been separated to form the so-called return coke-oven gas, and it is delivered to the consumer.

The solution of light oil in the wash oil is sent to a distillation tower, where the light oil is distilled off and the wash oil, after cooling, is returned to the light-oil scrubbers.

*Flushing liquor* contains dissolved ammonia and also the ammonium salts  $(\text{NH}_4)_2\text{CO}_3$ ,  $(\text{NH}_4)_2\text{S}$ ,  $\text{NH}_4\text{CN}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{CNS}$ ,  $(\text{NH}_4)_2\text{SO}_4$ , which form when the gas is cooled by reactions between ammonia and its other components. The flushing liquor is processed to recover the ammonia by heating it with steam and treating with milk of lime. The ammonia is stripped from the flushing liquor with live steam and is utilized for manufacturing ammonium sulphate. The phenols contained in the flushing liquor are also stripped from it with live steam and then absorbed by a sodium hydroxide solution to form phenolates.

*The light oil* is a complex mixture, the principal part of which boils off at temperatures up to  $180^\circ\text{C}$ . Average contents of the basic components of the light oil are: 1.6-3.4 per cent carbon disulphide and low-boiling hydrocarbons; 59.5-78.3 per cent benzene; 12-21 per cent benzene homologues; 3-10 per cent solvents (a mixture of trimethylbenzene, ethylmethylbenzene, etc.). Separation of the individual components of the light oil is based on differences in their boiling points and is carried out by distillation.

*The coal tar* contains about 300 different substances. The content of the most important substances in the tar (in %) is: naphthalene 5-10; phenanthrene 4-6; carbazole 1-2; anthracene 0.5-1.5; phenol 0.2-0.5; crezol 0.6-1.2; pyridine compounds 0.5-1.5. Besides these substances, the coal tar also contains small amounts of benzene hydrocarbons—benzene, toluene, xylenes; about 50-60 per cent by weight of the tar consists of high-boiling, high-molecular-weight products. The tar is separated by distillation into fractions and they are distilled to obtain benzene and its homologues and subjected to crystallization to separate out naphthalene and anthracene. Phenol is recovered from the various fractions by treating them with a sodium hydroxide solution to form sodium phenolate,  $\text{C}_6\text{H}_5\text{ONa}$ , which is then reacted with carbon dioxide to release the phenol. The pyridine compounds are removed from the fractions by washing them with dilute sulphuric acid.

The residue obtained when the tar is distilled—the coal-tar pitch—is utilized in manufacturing electrodes for electrolyzers and electric-arc furnaces, in road construction, as a protective coating for insulating electric power lines and underground pipelines.

*The return coke-oven gas* has approximately the following composition: 54-59 per cent  $\text{H}_2$ ; 23-28 per cent  $\text{CH}_4$ ; 5.0-7.0 per cent  $\text{CO}$ ; 2-3 per cent heavy hydrocarbons; 3.0-5.0 per cent  $\text{N}_2$ ; 1.5-2.5 per cent  $\text{CO}_2$ ; 0.3-0.8 per cent  $\text{O}_2$ . The calorific value of the gas is 16 700-17 200 kJ/m<sup>3</sup>.

The problems with which coke-chemistry engineers are faced at the present time can be summarized shortly as: (1) intensification of the carbonization process by creating continuous-action coke ovens, (2) extending the raw-material resources for the coking process by utilizing readily available grades of coal, (3) widening the assortment of products, (4) developing rational schemas for more complete and economic recovery of the components of the light oil, coal tar and coke-oven gas, (5) producing pure individual substances from the light oil and coal tar.

### 3. An Outline of Low-Temperature Carbonization of Coal and Shale and Dry Distillation of Wood

Low-temperature carbonization, sometimes called semicoking, is a process of thermal decomposition of fuels in the absence of air in direct- or indirect-heated ovens in which the final temperature reaches 500-550 °C.

**Low-temperature carbonization of coal** yields as its products low-temperature coke, coke-oven gas, tar and flushing liquor (which is not utilized).

*Low-temperature coke* is a very weakly sintered, friable product which contains considerable amounts of volatile matter (up to 10 per cent) and which is highly reactive. Low-temperature coke is ordinarily utilized as a local, energetics fuel.

*The semicoke oven gas*, which is produced in amounts of 100-120 m<sup>3</sup> per ton of coal processed, has a high content of methane and its homologues and relatively large hydrogen content. Its calorific value lies between 14 600 and 36 400 kJ/m<sup>3</sup>, depending on the nature of the coal raw material. Semicoke gas is used as a domestic gas, for heating industrial furnaces, etc. and also as a source of hydrocarbon raw materials in chemical synthesis.

*Low-temperature coking tar* is a dark, reddish-brown liquid which contains paraffin-, olefine-, haphthene-, aromatic- and other compounds. Low-temperature coking tar can be processed into liquid motor fuels and other hydrocarbon mixtures.

Consequently, the low-temperature carbonization process is carried out primarily for the purpose of obtaining tar and gas. In the USSR, which has great resources of petroleum and natural gas, it is more economical to utilize them for producing various kinds of liquid fuels and raw materials for the chemical industry.

**Low-temperature carbonization of shales.** A specific feature of this process is a high yield of tar. Coke, gas and flushing liquor are also produced. The yield of the various products in low-temperature coking of Estonian shale (from the Kokhtla-Yarve field), in per cent by weight of the dry shale, averages: 34.4 per cent tar, 55.8 per cent low-temperature coke, 1.5 per cent liquor. The gas yield is ~ 68 m<sup>3</sup>/t.

*Shale tar* is a complex mixture and it is processed in the same way as petroleum (see page 185). Motor fuels, solvents and other products are manufactured from the shale tar.

Due to the high ash content of the raw material the *coke* contains only 10 per cent carbon; the remainder consists of mineral substances—calcium oxide, silica, etc. and it can be used as a raw material for manufacturing cements.

*The gas* is utilized for heating the coke ovens.

**Dry distillation of wood.** The process of dry distillation of wood occurs in the following way: at first the moisture is removed by heating in the absence of air, at 170-270 °C gas (CO and CO<sub>2</sub>) formation begins and also formation of small amounts of acetic acid and methyl alcohol. Below 270-280 °C the reactions are endothermic, above this temperature exothermic reactions begin. Under such conditions the formation of vapour-phase products, CH<sub>3</sub>COOH and CH<sub>3</sub>OH and gases is accelerated. Between 280 and 400 °C the distillation of the volatile substances is completed. These processes result in formation of charcoal, and cooling the gas-vapour mixture produces wood tar, wood distillate and uncondensable gases. The yield of the various products depends on the kind of wood employed, the temperature and duration of the process.

*The charcoal* is used in metallurgy as a high-quality fuel which does not contain sulphur or phosphorus, and also for making activated charcoal, which is extensively employed as an adsorbent and as a reducing agent in a number of chemical manufacturing processes, etc.

*Wood tar*, whose most important constituents are various phenols and their methyl ethers, is used for impregnating wood, to protect it from rotting, as a raw material in manufacturing pharmaceuticals, in making flotation agents, anti-oxidants (inhibitors) for cracking gasoline, etc.

*The distillate* contains formic, acetic, propionic, and other acids, acetone, methylethylketone, methyl alcohol, acetaldehyde, furfural and other substances. At modern plants the methyl alcohol is stripped from the water distillate and the acetic acid is extracted with ethyl ether. For many years the wood chemical industry was the only source of these products. The development of industrial synthesis of acetic acid and methanol resulted in more economical and high-capacity processes for their production.

#### 4. The Processing of Liquid Fuels (Petroleum and Petroleum Products)

Petroleum and the products obtained by processing it are the most important liquid fuels. Petroleum treating processes have been in use for a long time. Approximately up to 1885 petroleum was distilled



to produce kerosene, used for lighting purposes, the remainder being employed as a furnace fuel. When automobiles, and later airplanes, came on the scene at the beginning of this century, this created an evergrowing demand for petrol, and later still developments in the chemical industry created a demand for new raw materials. The source of the raw materials was found in petroleum. Industrial petrochemical synthesis came into being; its characteristic features are deep changes in the petroleum and the accompanying gases as a result of which not only various types of fuels and lubricants, but also materials for making plastics, chemical fibres, synthetic rubbers, detergents, etc. are produced. In order to develop deep petroleum processing methods it was necessary to study the composition and properties of various kinds of petroleum, the behaviour of hydrocarbons during the processing operations, catalytic processes of hydrocarbon conversion, and a number of other problems.

*The products of the petroleum refining process* are fuels—gaseous and liquid, lighting kerosenes, solvents, lubricants, greases, solid and semi-solid mixtures of hydrocarbons—paraffin, ceresin, vaseline, etc.; petroleum bitumens and pitches, petroleum acids and their derivatives—alkaline naphthenates, sulphoacids, fatty acids, etc., individual hydrocarbons—ethylene, propylene, methane, benzene, toluene, xylene and others—which serve as raw materials for the chemical industry.

The most important of these, according to the scale of their production, are liquid and gaseous fuels and lubricants, and, in recent years, individual hydrocarbons.

Liquid petroleum fuels, depending on their use, are classed as: carburetor motor- (aviation, automobile and tractor petrol), jet- (for jet and turbojet engines), diesel-, gas-turbine- and furnace fuels. *Petrols* must possess definite properties: they should have a given fractional composition, vapour pressure, detonating properties; they must be chemically stable, and not corrosive. The fractional composition is described by the temperatures at which boiling begins and ends for fractions produced by distilling the petrol in the interval 25-200 °C. The vapour pressure should not exceed a definite limiting value.

The detonating properties of a petrol are very important. In the cylinder of an internal combustion engine a mixture of petrol and air is first compressed and then ignited by a spark created by a spark plug. The gases formed by combustion of the fuel drive the piston. The higher the degree of compression of the gas mixture in the cylinder, the higher will the engine efficiency be. However, the degree of compression is limited by the process of combustion of the mixture in the cylinder. The rate at which the flame spreads through the gas in the cylinder, when the mixture is ignited by a spark, varies. Under normal conditions, the rate of flame propagation is 10 to

15 m/sec, however, at a certain level of compression the mixture detonates, and the flame-propagation rate rises to 1500-2500 m/sec. Detonation results in knocking and overheating of the cylinder, dark exhaust gases are produced, fuel consumption rises, motor power is lowered, and wear increases.

The detonating properties of a petrol are described by its octane number. The petrol octane number is determined by comparing its detonation during compression in a cylinder of an internal combustion engine with that of a standard mixture, consisting of isooctane (2,2,4-trimethylpentane) and *n*-heptane, under similar conditions. It is arbitrarily assumed that isooctane, which does not detonate easily, has an octane number of 100, and *n*-heptane, with an extremely high tendency to detonate, an octane number of 0. The octane number of a petrol will then be equal to the content of isooctane in a standard mixture which detonates at the same compression as the petrol being tested. If, for example, the anti-knock value of a petrol was found to be equal to that of a mixture containing 80 per cent isooctane and 20 per cent *n*-heptane, its octane number will be 80. Petrols more stable than isooctane have octane numbers above 100.

Automobile petrols have octane numbers of 76 to 95. Aviation petrols, for planes with piston engines, are manufactured with octane numbers above 100.

The octane number of a fuel depends on its composition—it is increased by the presence of isoparaffins and aromatic compounds. One of the methods for increasing the anti-knock value of petrols, i.e. a method for making high-octane motor fuels, is isomerization and aromatization of hydrocarbons contained in them. High-octane motor fuels can also be obtained by mixing the base petrol, i.e. straight-run petrol or cracking with high-octane components—*isooctane*, *isopentane*, *ethylbenzene*, *isopropylbenzene*, etc.

Anti-knock agents may be added to petrols to increase their octane number; the most extensively employed is tetraethyl lead— $\text{Pb}(\text{C}_2\text{H}_5)_4$ , a component of so-called ethyl fluid. Adding 4 ml of ethyl fluid to 1 kg of petrol, for instance, raises the octane number of a petrol from 70 to 89. Ethyl fluid is poisonous, and ethylated petrol containing it should be handled with care.

Chemical stability describes the tendency of a petrol to form tar and to change chemically during storage or in the internal combustion engine. It depends on the composition of the fuel and it is lower if there are olefines and diolefines present. The corrosive effect grows with an increase in sulphur content and acidity of a petrol.

*Tractor fuel*, mainly kerosene, is described by the same characteristics as motor petrol. The octane number of kerosene should not be under 40.

*Diesel fuels*—kerosene, gas-oil, solar distillate—are made for use in internal combustion piston engines in which ignition results from

the compression of the gas. Economic operation of Diesel motors depends on the fractional composition and cetane number of the Diesel fuel. A Diesel fuel should consist mainly of a narrow fraction which boils, usually, from 200 to 350 °C. The cetane number characterizes the capability of a fuel to ignite in the motor cylinder; the larger the number, the better is the fuel. The cetane number is determined by comparing the behaviour of a Diesel fuel in a motor with the behaviour of a standard mixture of cetane ( $C_{16}H_{34}$ ), whose cetane number is assumed to be 100, and  $\alpha$ -methylnaphthalene ( $C_{10}H_7CH_3$ ), whose cetane number is assumed to be 0.

*Furnace fuel oils* are mazout and other distillation residues. If mazout is not utilized for making lubricants, petrol or other motor fuels, it is burned in furnaces of locomotives, steam boats, power plants, etc. and also in industrial furnaces.

*Jet engine fuel* is a kerosene fraction and it is used for powering jet engines.

*Gaseous petroleum fuels* include casing-head gas and the gases produced by processing petroleum and petroleum products.

*Lubricating oils* can be divided into groups with respect to their applications: industrial oils—spindle oil, machine-lubricating oils, etc.; oils for internal combustion engines—motor and tractor engine oils, aviation lubricating oils, etc.; transmission oils, turbine oils, compressor oils; oils for steam engines—cylinder oils, and special-purpose oils.

The quality of an oil is determined by its lubricating property, viscosity, solidification temperature and flash point, density, moisture content, acidity, tendency to coke, ash content and stability.

**Preliminary petroleum processing.** Preliminary processing of the petroleum consists in removing dissolved gases, mineral salts, moisture and mechanical impurities—sand and clay—from the crude petroleum. Impurities are removed in part at the well and in part at the petroleum-refining plants.

*Gases are removed* in traps, in which both the pressure and the velocity of the petroleum stream are reduced, so that the dissolved gas is liberated. In many cases together with the dissolved gas the so-called natural gasoline, the lightest hydrocarbon mixture, is also separated. The natural gasoline is removed from the gas by absorbing it with solar oil or adsorbing it on activated charcoal.

*Mineral salts* are removed in a desalting process, which consists of scrubbing the petroleum repeatedly with warm water to dissolve the salts. The emulsion formed during this scrubbing process is separated from the petroleum during dehydration.

*Dehydration* can be carried out by lengthy settling and part of the physical impurities are then removed together with the water. However, since petroleum forms highly stable emulsions with water, complete dehydration is only possible if the emulsion is destroyed by

introducing de-emulsifying reagents into the petroleum under heating (for example, sodium salts of naphthenic acids). A very efficient method is that of electrical dehydration, which consists in passing a film of petroleum at a high temperature between electrodes to which alternating current is fed at a voltage of 30 000-40 000 V; this destroys the emulsion, the water-drops coagulate, and then the water is separated from the petroleum by settling.

*Stabilization* of the petroleum follows the operations of desalting and dehydration. This process lowers losses of light hydrocarbons during transportation and storage and also provides a constant level of the vapour pressure. Stabilization is achieved by stripping the propane-butane, and in some cases also part of the pentane fraction of the hydrocarbons. The stabilization unit is equipped with furnaces for heating the petroleum and a distillation tower for separating the propane-butane fraction, which is a valuable raw material for the chemical industry.

**The principal petroleum-processing methods and apparatus.** Depending on the kind of products to be obtained from the petroleum, one of the three processing modes is employed: *fuel-processing*, which yields motor and furnace fuels; *fuel-lubricant processing*, in which both fuels and lubricants are the products and *petrochemicals (integral) processing*, by which not only fuels and lubricants are produced but also raw materials for the chemical industry — olefines, aromatic and paraffinic hydrocarbons, etc. In these different processes for treating petroleum common methods are used. The methods can be divided into two classes: physical ones and chemical ones.

*The physical processing methods* produce individual hydrocarbons or, more often, their mixtures from the petroleum or petroleum products, utilizing differences in their physical properties, i.e. boiling point, crystallization temperature, solubility, etc. The most extensively employed method is so-called straight-run distillation of petroleum and petroleum products, i.e. separation of petroleum into fractions with different boiling points.

*The chemical methods* are based on deep, chemical, destructive transformations of the hydrocarbons contained in the petroleum or petroleum products, effected by temperature, pressure, or catalysts. Most extensively used are various forms of cracking.

Petroleum processing employing *catalytic conversion* techniques is also now used.

*The apparatus* for treating petroleum and petroleum products serve first of all for heating them to a high temperature, then for dividing the products obtained, and, when required, for carrying out catalytic reactions. For heating the petroleum and petroleum products pipe furnaces are employed. Heat is transferred from gaseous combustion products to the pipes, through which the liquid materials flow, by radiation and by convection.

The surface area of the radiant tubes,  $F_r$  ( $\text{m}^2$ ), can be determined from the equation

$$F_r = \frac{Q_r}{\sigma_r} \quad (8.4)$$

The surface area of the convection tubes,  $F_c$ , is calculated using the equation

$$F_c = \frac{Q_c}{\Delta t_m k_t} \quad (8.5)$$

where  $Q_r$  and  $Q_c$  are the amounts of heat which are transferred to the tubes by radiation and convection, respectively,  $\text{kJ/hr}$ ;  $\sigma_r$  the

thermal intensity of the radiant tubes,  $\text{kJ/m}^2 \cdot \text{hr}$ ;  $\Delta t_m$  the mean logarithmic difference of the temperatures of the raw material and the combustion gases in the convection chamber,  $^{\circ}\text{C}$ ;  $k_t$  the heat-transfer coefficient,  $\text{kJ/m}^2 \cdot \text{hr} \cdot \text{deg}$ .

Usually  $\sigma_r$  lies between 60 000 and 160 000  $\text{kJ/m}^2 \cdot \text{hr}$  and  $k_t$  is equal to 85-170  $\text{kJ/m}^2 \cdot \text{deg} \cdot \text{hr}$ .

At present flameless-combustion pipe furnaces (Fig. 65) are used for heating petroleum and petroleum products. The furnace is made of prefabricated ribbed panels. There is a layer of heat insulating bricks between the ribs of the panels which keeps the outside wall temperature at about  $45^{\circ}\text{C}$ . The liquid materials flow through tubes joined in series. They first pass through tubes 6 in the convection heating chamber and then enter the radiant heating tubes 2, 1, 5. These tubes are located along the partition walls, the hearth and roof of

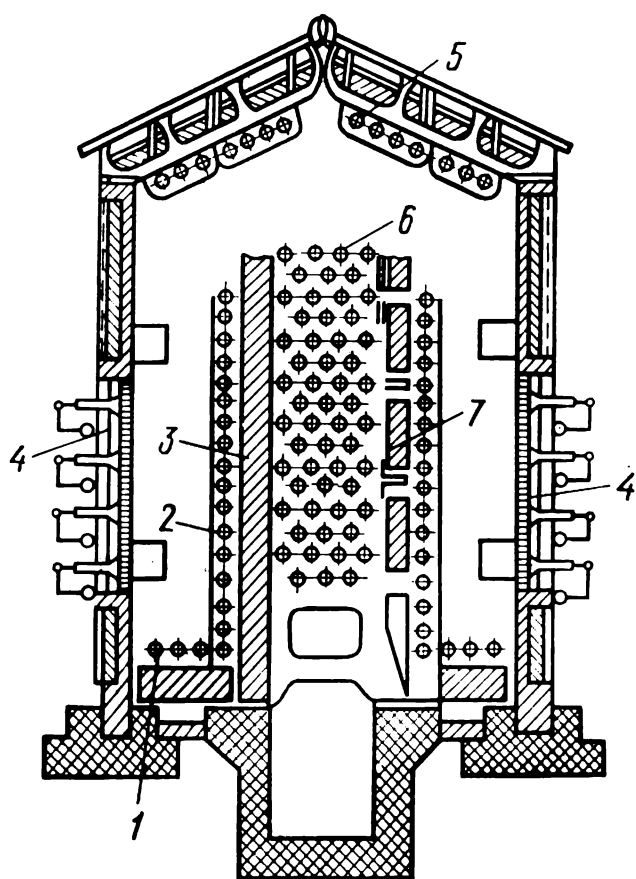


Fig. 65. Flameless-combustion pipe still:

1, 2, 5—radiant heating tubes; 3, 7—partitions; 4—burners; 6—convective heating chamber tubes

the furnace. The furnace uses a gas fuel which is fed to prism-shaped ceramic burners in the furnace walls. By flameless combustion of the gas fuel in the burners the ceramic plates are heated to incandescence and heat is intensely radiated to the surface of radiant tubes. The gaseous combustion products flow through the convection chamber and transfer heat by convection to the tubes carrying the material on its way to processing. A feature of modern pipe furnaces is a high degree of utilization of the excess heat of the off-gas com-

bustion products and the heated liquid, which are used to produce steam.

There are flameless combustion furnaces with vertical radiant tubes.

The products of petroleum processing are mainly separated by distilling them in towers of various types. Most commonly employed are various types of bubble-cap tray towers. A distinct feature of petroleum-refining distillation towers is that they consist of a number of primary, independent columns placed one above the other with liquid products removed at various heights. The liquid enters into stripping sections, located outside the tower, where steam is passed through it. This produces vapours of the low-boiling fractions, which are returned to the tower, and also a liquid petroleum product, or distillate. Distillation towers are operated under pressure, at atmospheric pressure or under vacuum.

The catalytic processes of petroleum-refining units are carried out in reactors of different designs. As a rule, the catalyst in these processes quickly loses its activity, and catalytic-converter units, therefore, include both reactors and regenerators. The reactors and regenerators may be with the catalyst in a filtering bed, a fluidized bed or with a moving catalyst.

Along with the basic apparatus, refining units contain heat exchangers, condensers, storage tanks and other equipment.

**Physical petroleum-refining methods (straight-run distillation).** Distillation of petroleum, which is based on the differences in the boiling points of the various petroleum fractions, produces the fractions or distillates, listed in Table 10.

TABLE 10

Petroleum Fractions (Distillates)

Distillate	Draw-off temperature, °C	Approximate yield, % by weight of petroleum *
Petrol	up to 170	14.5
Ligroine	160-200	7.5
Kerosene	200-300	18.0
Gas oil	300-350	5.0
Remainder (mazout)	—	55.0

\* The yields are for methane petroleum from the Grozny field.

Each of these fractions can in turn be redistilled and separated into fractions with a narrower range of boiling points, producing

different kinds of distillates. Petroleum distillation is carried out under atmospheric pressure. The remainder obtained in the distillation process—mazout (fuel oil)—can also be subjected to fractionation. Vacuum must be employed in distilling the mazout, to avoid decomposition of the hydrocarbons contained in it at high temperatures. This operation yields the distillates of Table 11.

TABLE 11

## Mazout Fractions (Distillates)

Distillate	Draw-off temperature, °C *	Approximate yield, % by weight of the petroleum
Spindle oil	230-250	10-12
Machine oil	260-305	5
Light cylinder oil	315-325	3
Heavy cylinder oil	350-370	7
Residual asphalt	350-370	27-30

\* The draw-off temperature at an absolute pressure of 60-80 mm Hg.

The distillates obtained by distilling mazout are raw materials for making lubricants. At the present time petroleum and mazout are distilled in so-called pipe-still units, where the following sequence of operations takes place: preheating of the raw material by interchange with the distillation products in heat exchangers (recuperation); the main stage of heating the raw material in the pipe still; separation of the vapours formed from the liquid remainder, and their distillation in distillation towers, condensation and cooling of the distillation products in coolers, which also serve as raw-material heaters. The petroleum distillation units can be single-stage ones, in which fractions ranging from petrol up to high-boiling fractions are produced from the petroleum at the atmospheric pressure, and two-stage ones, in which the petroleum is first distilled at atmospheric pressure to obtain petrol, ligroine, kerosene, gas oil and mazout, and then lubricating-oil distillates are separated from the mazout under vacuum. Two-stage units for petroleum distillation are called atmospheric-vacuum units.

A representative flow diagram of a single-stage unit is given in Fig. 66.

A pump forces the petroleum consecutively through shell-and-tube heat exchangers 4, where it absorbs heat from the distillates and is heated to approximately 170-175 °C, and then through the tubes of

the first pipe still 1. The petroleum in the tubes is under a small excess pressure created by the pump. From the pipe still the petroleum at a temperature of 300-350 °C and in a liquid-vapour state is fed to the lower part of the distillation tower 2, where the pressure is lowered, and the volatile fractions evaporate and separate from the liquid remainder, the mazout. The vapours of these fractions rise up through the column and are distilled. At various heights distillates are removed in a condensed state; they are in turn subjected to distillation in stripping towers (not shown in Fig. 66) and cooled first in exchangers 4 by the petroleum entering the unit and then with water in coolers 3. Petrol vapours are removed at the top of the column and are cooled in condenser 3, where they are converted into liquid. Part of the liquid petrol is returned to the column as reflux. A two-stage unit consists of two similar blocks—a block of straight-run petroleum refining (Fig. 66) and a second block for separating mazout into fractions. The mazout, which is removed at the bottom of the tower, is delivered to a pipe still, where it is heated to 400-420 °C, and is then transferred to a tower which operates under vacuum. From the lower part of the tower residual asphalt is removed and lubricant distillates are withdrawn at several heights. The petrol yield of straight-run distillation depends on the composition of the petroleum and lies between 3 and 15 per cent.

Straight-run petrols consist mainly of paraffinic and naphthenic hydrocarbons; petrols obtained from petroleum with a high aromatic-hydrocarbon content are an exception. The octane number of the petrols (depending on their composition) is from 50 to 78. By adding ethyl fluid, petrols with octane numbers up to 87-95 are obtained.

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**High-temperature chemical processing of petroleum and petroleum products.** High-temperature chemical processing of petroleum and petroleum products is a method for destructive treatment of petroleum, which leads to more or less intensive changes in the molecular structure of the initial materials. One such process is cracking of

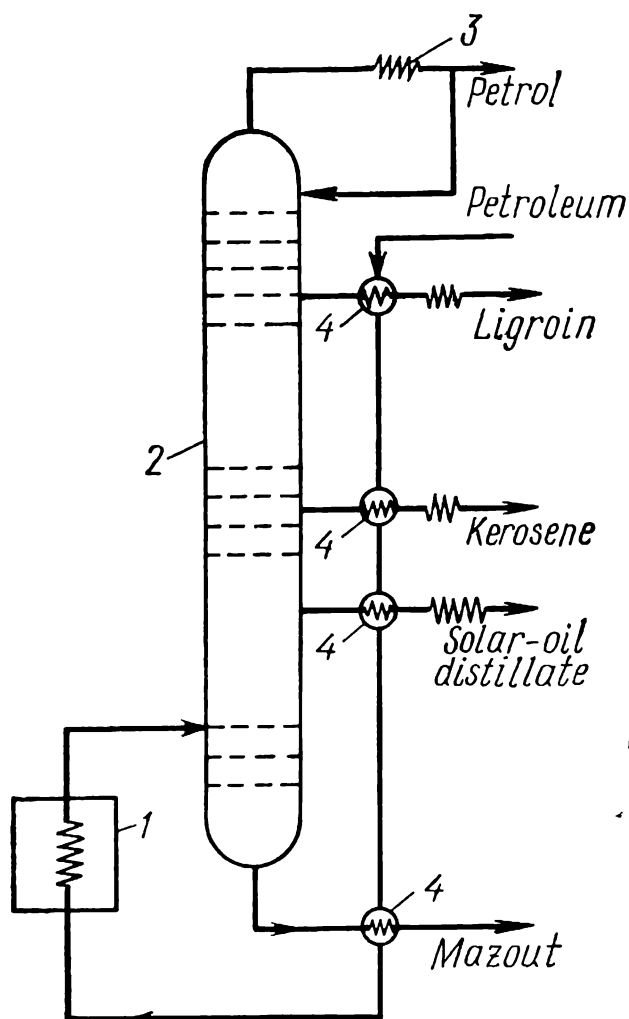
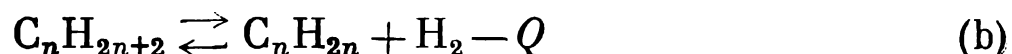


Fig. 66. Schematic diagram of a petroleum distillation unit

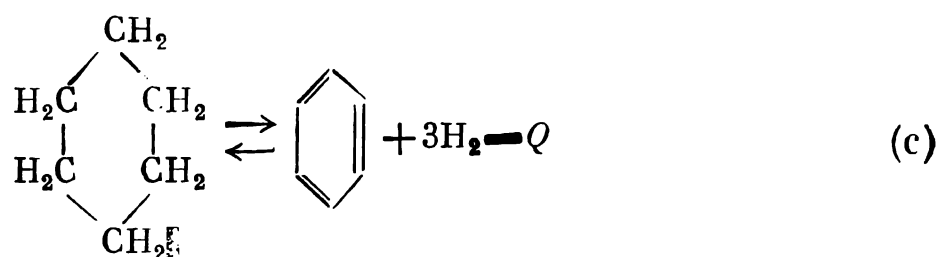


petroleum distillation fractions (from ligroine to mazout). Cracking is the splitting of molecules of the initial material into smaller ones. Along with the processes of decomposition, cracking is accompanied by secondary processes of synthesis of larger molecules. Reforming is the cracking of low-octane petrol or ligroine to raise the octane number of a carburetor fuel or to obtain hydrocarbons for organic synthesis. Cracking and reforming at high temperatures without a catalyst are called *thermal cracking*, and *thermal reforming*; when a catalyst is used, they are correspondingly called *catalytic cracking* or *catalytic reforming*. Thermal cracking is carried out at 470-540 °C and at pressures of up to 60 atm.

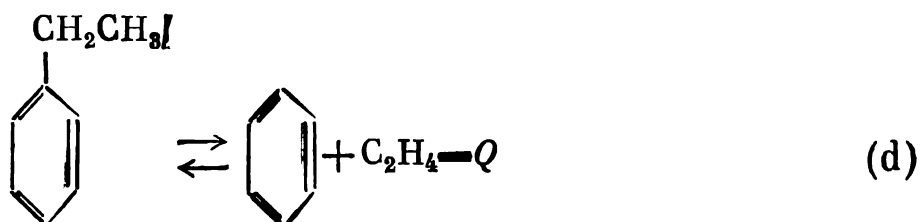
In spite of the complex nature of hydrocarbon conversions during cracking, some of the rules governing the behaviour of various hydrocarbon groups have been discovered. At high temperatures rupture of the molecular chains and dehydrogenation of methane hydrocarbons can occur



The olefines formed undergo further transformations. When naphthene hydrocarbons are dehydrogenated aromatic hydrocarbons are formed, for example, dehydrogenation of cyclohexane produces benzene:



Aromatic hydrocarbons may rupture at the  $C_{aryl} - C_{alkyl}$  bond and split off a side chain. This produces simple aromatic and unsaturated hydrocarbons, for example ethylbenzene yields benzene and ethylene by the reaction:



Condensation of the aromatic hydrocarbons, which results in coke formation, is also possible. The unsaturated hydrocarbons produced in the cracking process enter into condensation, alkylation, and cyclization reactions with each other and with the initial substances to form aromatic and other complex hydrocarbons.

Hydrocarbon reactions often take a chain mechanism. To determine the nature of the products obtained by cracking, one must know which of the reactions of hydrocarbon conversion are more probable according to the reaction thermodynamics. Fig. 67 shows the change in the free energy of formation of some hydrocarbons with temperature from 300 to 1200 °K. The relative stability of the hydrocarbons can be determined from these data. At higher temperatures the

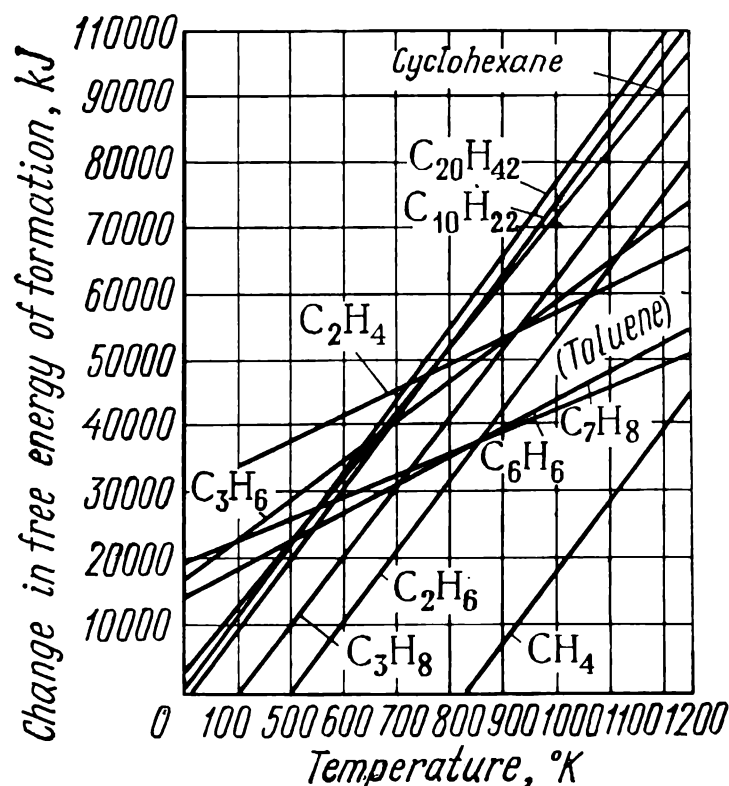


Fig. 67. The change in the free energy of hydrocarbon formation (per carbon atom) with temperature

strength of the hydrocarbon bonds is lower. Fig. 67 shows that at all temperatures methane is more stable than other compounds; the thermal stability of the paraffin hydrocarbons of a homologous series decreases as the size of the molecules grows. This means that upon heating the hydrocarbons with longer chains split first. The split position shifts towards the end of the chain with an increase in the temperature and this leads to formation of more stable, short-chain hydrocarbons, up to methane. However, at temperatures above 820 °K methane also begins to decompose into carbon and hydrogen.

At low temperatures (below 500 °K) the methane and naphthene hydrocarbons are more stable, whereas at high temperatures the aromatic hydrocarbons and olefines are the most stable. Therefore, at high temperatures they will accumulate in the cracking product. Fig. 67 does not answer the question, which of the reactions, (a) or (b), is most probable from the point of view of thermodynamics. For a dehydrogenation reaction the change in the free energy is:

$$\Delta F = 130 - 0.14T \text{ kJ/g-mole} \quad (8.6)$$

For a reaction resulting in rupture of the carbon chain it is:

$$\Delta F = 80 - 0.14T \text{ kJ/g-mole} \quad (8.7)$$

It follows from equations (8.6) and (8.7) that chain rupture is more probable than dehydrogenation. A thermodynamic analysis of the process shows that a given change in the cracking temperature promotes one certain reaction of the number of them which are ther-

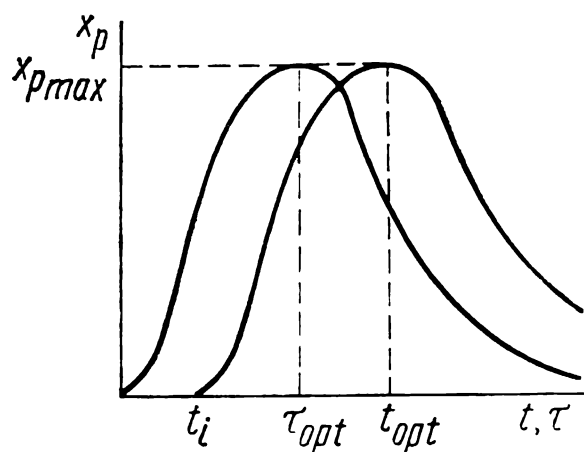


Fig. 68. Petrol yield vs temperature and residence time

modynamically possible. Along with this, the temperature has a significant effect on the process rate, since cracking is kinetics limited.

The dependence of the reaction rate on the temperature is expressed by the Arrhenius equation. The temperature coefficient of the reaction,  $\beta$ , is about two. The activation energy for paraffinic and naphthenic hydrocarbons amounts to about 200-300 kJ/mole, and for aromatic ones to 300-400 kJ/mole. Because

of this, according to the rate of their conversion, hydrocarbons are arranged in the following order: paraffinic, naphthenic, aromatic.

It is very difficult to give an overall kinetics equation for the process which fully reflects the diversity of all the reactions taking place with sufficient accuracy. Nevertheless, the cracking rate can be approximately described by a first-order equation:

$$u = \frac{dx}{d\tau} = k_m (a - x) \quad (8.8)$$

where  $k_m$  is the mean rate constant of the reaction. Equation (8.8) describes reactions of primary decomposition of paraffin hydrocarbons and higher olefines and of dealkylation. However, the mean rate constant of the reaction,  $k_m$ , decreases as the process continues. This results from the appearance of secondary reactions and a drop in the rate of decomposition of stable molecules of the raw material. Thus, at constant temperatures and pressure,  $k_m$  decreases with time.

The most important of the products manufactured at most plants is petrol. At some temperature,  $t_1$ , decomposition of the less stable heavy hydrocarbons begins and lighter hydrocarbons which are a part of the composition of petrol are formed. As the temperature rises (Fig. 68) the process rate grows and the petrol yield,  $x_p$ , (for constant residence time in the reactor and constant pressure) grows. However, raising the temperature further leads to decomposition

of the lighter hydrocarbons to form gases. It follows, that there should be a certain optimal temperature with a maximum petrol yield.

The pressure does not affect the rate of decomposition of hydrocarbons. On the one hand, a pressure rise slows down reversible cracking reactions which result in formation of gaseous products and thus increases  $x_p$ ; on the other hand, it favours secondary reactions which give rise to heavy products and decrease the yield of petrol. Therefore, the curve for the  $x_p = f(P)$  function is similar to that for the  $x_p = f(t)$  function (see Fig. 68) and has a maximum, corresponding to the largest petrol yield. Consequently, if it is desired to increase the yield of liquid products the process is carried out at high pressures, and if, on the contrary, it is necessary to obtain large amounts of gases, cracking should be carried out at a low pressure.

The residence time of the hydrocarbons in the high-temperature zone affects the course of cracking reactions. The nature of the change in the petrol yield with time at comparatively high cracking temperatures is shown in Fig. 68. When the residence time of the products in the high-temperature zone is increased (at  $P, t = \text{const}$ ) the degree of decomposition of the heavy hydrocarbons rises and the yield of petrol grows with it. A further increase in the residence time  $\tau$  results in fission of the lighter hydrocarbons and formation of gases, and the  $x_p$  value drops.

Because of this the degree of conversion during one passage through the cracking apparatus is limited to 50-70 per cent. Then, after the cracking products, e.g. petrol and a heavy remainder, are removed, the so-called intermediate fraction is again subjected to cracking, either separately or in a mixture with fresh raw material (cracking with recirculation, or recycle).

Thermal cracking yields petrol, gases and cracking remainder as its products. Thermal cracking can be of two kinds: two-phase, vapour-liquid (formerly called liquid-phase cracking) and vapour-phase cracking. The first of these is carried out at a temperature of 470-540 °C and a pressure of 40 to 60 atm, the second, at 550 °C and higher under pressures of 2-5 atm. The cracking reactions of liquid-phase cracking processes take place both in the liquid and the vapour phase, and those of vapour-phase cracking in the vapour phase.

Basically, the technological process consists of heating the raw material in pipe stills to a temperature at which cracking of the hydrocarbons proceeds at a sufficiently high rate, and separating the cracking products by rectification. This method is extensively employed for processing heavy petroleum-distillation residues. Thus, for example, thermal cracking of mazout yields on the average the following products: 30-35 per cent cracking petrol, 10-15 per cent cracking gas, 50-55 per cent cracking residue.

Thermal-cracking petrols have higher anti-knock values than some of the straight-run petrols, due to the presence in them of aromatic

hydrocarbons and hydrocarbons with a branched-chain structure. The octane number of such petrols is about 70. Because of the presence of highly reactive unsaturated hydrocarbons in cracking petrols, they are less stable than straight-run petrols. Thermal-cracking gas is a mixture of saturated and unsaturated hydrocarbons: ethane, ethylene, propane, propylene, butanes, butylenes, pentanes, and others. The cracking residue is mainly employed as a fuel.

*Pyrolysis* of kerosene or other petroleum products is carried out by vapour-phase cracking at a temperature of about 650-720 °C and at nearly atmospheric pressure. The high temperatures used in the process result in formation of large amounts of gaseous products rich in ethylene and other unsaturated hydrocarbons and in aromatic hydrocarbons which are a raw material for organic syntheses.

*Catalytic cracking*, i.e. cracking carried out in the presence of catalysts, gives a higher yield of petrol and distillates from a heavy crude petroleum; the petrol produced has a higher octane number; and along with the petrol, large amounts of light,  $C_3$ - $C_4$ , hydrocarbons (gases) are obtained. When a sulphurous raw material is subjected to catalytic cracking the petrol formed has a low sulphur content, since the sulphurous compounds pass over into the gas phase. As a result of these positive features catalytic cracking has become one of the most widespread methods used in industrial processing of petroleum and petroleum products.

The use of a catalyst reduces the activation energy of the cracking reactions, and as a result, the rate of catalytic cracking is considerably higher than that of thermal cracking. Thus, catalytic cracking of naphthenes proceeds at a rate 500-4000 times higher than that of thermal cracking. At present these positive features of catalytic cracking have made it the most important of the methods used for destructive processing of petroleum and petroleum products.

Catalytic cracking is carried out in the vapour phase at a temperature of 450-520 °C, pressure of 1-2 atm, and with a time of contact between the raw-material vapours and the catalyst of several seconds. Porous aluminosilicates, mainly synthetic ones which are good adsorbents, are employed as the catalysts. The catalysis process consists of the following elementary acts: diffusion of the starting materials to the catalyst surface, their adsorption on the catalyst, formation of intermediate complexes at the catalyst surface, formation of cracking products, desorption of the cracking products from the catalyst surface, and their diffusion—first inside the catalyst pores and then into the free space. The chemical processes which take place over a catalyst are of a chain nature. They are accompanied by homogeneous, thermal decomposition of the hydrocarbons.

If the catalyst grains are small in size the limiting stage of catalytic cracking is probably that of adsorption of the hydrocarbons on the catalyst surface and, therefore, the order in which the different

kinds of hydrocarbons are cracked depends on their capability to adsorb on the surface.

In catalytic cracking the most stable compounds are normal paraffinic and aromatic hydrocarbons whose molecules do not contain side chains. Olefines, naphthenes, aromatic hydrocarbons with long side chains are less stable and crack easily. Aromatic hydrocarbons with side chains crack by separating the rings from the side chains, without disruption of the rings proper. This results in formation of the simplest aromatic and unsaturated hydrocarbons. Aromatic hydrocarbons exhibit a tendency to condense and form coke.

The unsaturated hydrocarbons formed in the cracking reactions are ruptured at carbon-carbon bonds, undergo isomerization, polymerization and aromatization. An important reaction is intermolecular redistribution of hydrogen, which consists in saturating olefines with hydrogen produced by formation of low hydrogen-content condensation products. The processes named above, on the one hand, produce stable petrols due to the low content of unsaturated hydrocarbons in them, but, on the other hand, form coke deposits on the catalyst surface.

Over aluminosilicates there is dehydrogenation and rupture of C—C bonds of naphthenic hydrocarbons; both with formation of open chains and with detachment of side chains. These transformations of the naphthenes produce aromatic hydrocarbons, which raise the octane number of the petrol, and also form a certain amount of condensation products part of which remain on the catalyst surface. Paraffinic hydrocarbons crack to yield both saturated and unsaturated compounds. The latter undergo secondary transformations.

The kinetics of catalytic cracking, just as that of thermal cracking, can be approximately described by a first-order equation of the type of (8.8). The reactions of hydrocarbon cracking form not only vapour-phase and gaseous hydrocarbons, but also solid coke deposited on the catalyst surface, which reduces contact between the catalyst and the molecules of the hydrocarbons and, consequently lowers its activity. To restore the activity, the catalyst is regenerated. This is accomplished by burning the coke covering the catalyst in an air stream at 550-600 °C, after which the catalyst is re-used in the cracking process. It follows that actually catalytic cracking consists of alternate processes of catalysis and catalyst regeneration.

The various *catalytic cracking processes* differ in the state of the catalyst bed. At present there are three types of units in use: with a stationary, filtering-bed catalyst, with a suspended, or fluidized, catalyst bed, and with a moving catalyst (see Part I, Chapter 6).

When a filtering bed is used the catalyst is regenerated by periodically discontinuing feed of the raw material and introducing air to burn the coke. Such catalytic-reactor units with an alternating

cycle operate at low intensity and have now been replaced by units with a suspended bed of the catalyst or a moving catalyst. In such units the cracking operation and regeneration process are carried out separately: cracking—in the catalytic reactor and regeneration in special regenerators, which do not differ significantly in design from the reactor. The catalyst continuously circulates through the reactor and the regenerator.

Cracking using a fluidized bed of catalyst, which is most extensively employed, is carried out using a spherical-pellet catalyst. In the flow diagram of Fig. 69 the reactor and regenerator are combined in one unit, in which the reactor at the top and the regenerator at the bottom are connected by pipes through which the catalyst flows. The stock charge, after passing through a pipe still (not shown in Fig. 69), entrains the regenerated catalyst from the cylindrical well and through a pipe it enters the reactor above the grate together with the catalyst. The reactor operation model is one of complete mixing of both the gas and the solid phases, which provides isothermal conditions. The cracking occurs in the reactor. In a cyclone catalyst particles are removed from the cracking products, which are then subjected to separation. The grains of the catalyst, which are covered with a layer of the coke formed in the reactor, flow to the stripper section, where they are treated with steam to peel off the coke. The

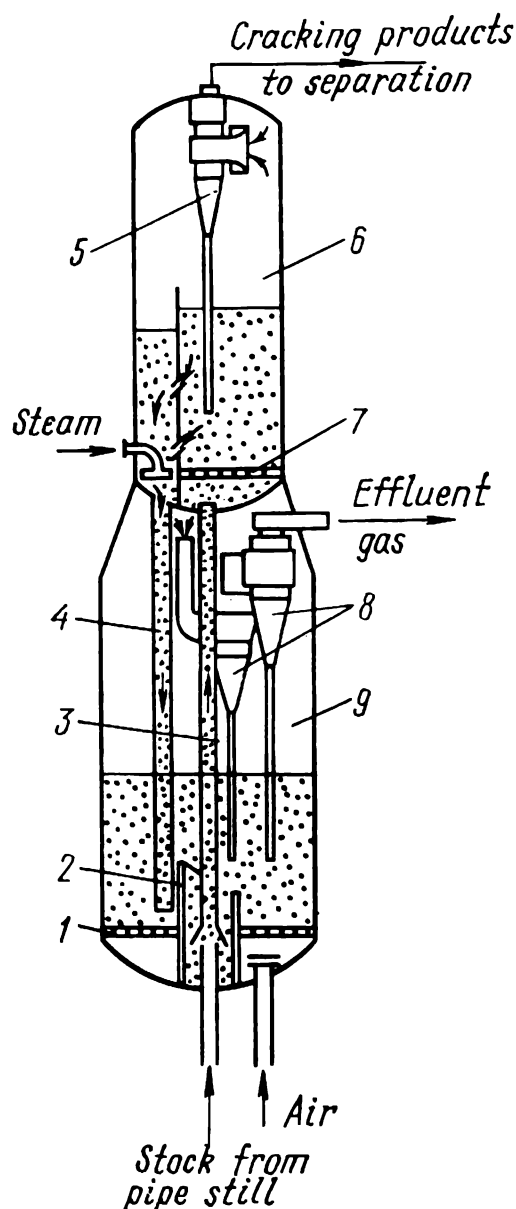


Fig. 69. Fluidized-bed catalytic cracking reactor:

1, 7—distribution grates; 2—well and ejector; 3, 4—catalyst ducts; 5, 8—cyclones; 6—catalytic reactor; 9—regenerator

steam—fed to the stripper at the bottom—also serves to create a vapour seal which prevents the cracking products from entering into the regenerator. The spent catalyst through a pipe passes down into the regenerator into which air for burning the coke is blown through the grate at the bottom. The combustion products, after being cleaned in a cyclone, are removed from the apparatus to a waste-heat boiler and the regenerated catalyst is recycled to the reactor. In the

regeneration process the catalyst temperature rises as a result of combustion of the coke and the raw material in contact with it in the reactor is heated. It follows that the catalyst also serves as a heating agent—its heat makes up for the heat lost in the endothermic cracking reactions.

The dimensions of the catalytic reactor and the regenerator depend on the capacity of the unit. Thus, the diameter of the catalytic reactor is described by the formula

$$D = \sqrt[4]{\frac{V_g}{\pi w_g}} \quad (8.9)$$

where  $V_g$  is the volume of the gas-vapour mixture passed through the reactor in unit time,  $\text{m}^3/\text{sec}$ ;  $w_g$  is the linear rate of flow of the gas-vapour mixture in the free space of the reactor,  $\text{m}/\text{sec}$ . The value of  $V_g$  depends on the depth to which cracking is carried out and is given by:

$$V_g = \left( \frac{G_g}{M_g} + \frac{G_p}{M_p} + \frac{G_h}{M_h} \right) \cdot \frac{22.4}{3600} \cdot \frac{273+t_c}{273} \cdot \frac{760}{P} \quad (8.10)$$

where  $G_g$ ,  $G_p$ ,  $G_h$  are the quantities of cracking gas, petrol, and heavy fraction produced and reflux used (in the distillation columns) respectively;  $M_g$ ,  $M_p$ ,  $M_h$ , the mean molecular weights of the gas, petrol, and heavy fraction, respectively;  $t_c$  the temperature of the fluidized catalyst bed in the reactor,  $^{\circ}\text{C}$ ;  $P$  the pressure of the gas-vapour phase in the reactor,  $\text{mmHg}$ .

The rate of flow of the gas-vapour raw material mixture, on the one hand, must not exceed a certain value,  $w_e$ , above which the catalyst particles are entrained from the bed and, on the other, should be high enough to form a suspended catalyst bed, i.e. to convert it to a fluidized state,  $w_f$ . The maximum flow rate is determined using the equation:

$$\text{Re}_e = \frac{\text{Ar}}{18 + 0.61 \sqrt{\text{Ar}}} \quad (8.11)$$

where  $\text{Re}_e$  is the Reynolds number corresponding to the rate of flow at which entrainment of the finest catalyst particles begins;  $\text{Ar}$  is the Archimedes number.

$$\text{Re}_e = \frac{w_e d}{\nu}$$

where  $d$  is the particle diameter and  $\nu$  the viscosity of the gas.

The minimum rate of flow of the raw-material stream,  $w_f$ , can be calculated using the formula

$$\text{Re}_f = \frac{\text{Ar}}{1400 + 5.22 \sqrt{\text{Ar}}} \quad (8.12)$$

where  $\text{Re}_f$  is the Reynolds number corresponding to the flow rate  $w_f$  at which the largest particles of the catalyst are suspended. The



Archimedes number is computed using

$$Ar = \frac{gd^3}{\nu^2} \cdot \frac{\rho_s - \rho_g}{\rho_g} \quad (8.13)$$

where  $g$  is the acceleration due to gravity;  $\rho_s$  and  $\rho_g$  the density of the solid particles (catalyst) and the gas.

The size of the reactor can be determined from the material balance and the operating conditions. As an example, the material balance of a reactor for catalytic cracking of a kerosene-solar oil fraction is given in the following table.

**The Material Balance of a Kerosene-Solar Oil Fraction in a Catalytic-Cracking Reactor**

In			Out		
Item	kg/hr	%	Item	kg/hr	%
Kerosene-solar oil fraction	50 000	100	Petrol	27 500	55
			Heavy fraction	13 000	26
			Cracking gas	7 000	14
			Coke	2 000	4
			Losses	500	1
Total	50 000	100	Total	50 000	100

In this process the catalyst temperature in the reaction zone is 450 °C, the pressure over the fluidized catalyst bed is 1050 mmHg. The mean molecular weights of the fractions are  $M_p = 110$ ,  $M_h = 260$ ,  $M_g = 32$ .

Using formula (8.10) the volumetric flow rate of the gas-vapour phase is calculated:

$$V_g = \left( \frac{G_g}{M_g} + \frac{G_p}{M_p} + \frac{G_h}{M_h} \right) \cdot \frac{22.4}{3600} \cdot \frac{273 + t_c}{273} \cdot \frac{760}{P} =$$

$$= \left( \frac{7000}{32} + \frac{27\,500}{110} + \frac{13\,000}{260} \right) \cdot \frac{22.4}{3600} \cdot \frac{273 + 450}{273} \cdot \frac{760}{1050} = 6.15 \text{ m}^3/\text{sec}$$

From the above, the reactor diameter at  $w_g = 0.3 \text{ m/sec}$  is found to be

$$D = \sqrt{\frac{4V_g}{\pi w_g}} = \sqrt{\frac{4 \times 6.15}{3.14 \times 0.3}} = 5.1 \text{ m}$$

The diameter of the regenerator is determined in a similar fashion.

*In cracking with a moving catalyst* two basically different methods for transporting the catalyst are used: the catalyst grains drop down through a stream of the raw material subjected to cracking, or the

catalyst is moved up to the top of the apparatus by a gas stream, i.e. in the form of a suspension in the stream (pneumatic conveyer). In one of the widely used schemes of catalytic cracking both types of catalyst motion are employed (Fig. 70). The raw material is heated in a pipe still and enters at the top into the catalytic reactor, to which the catalyst pellets are fed from a bunker. The cracking products are removed from the reactor for separation. The catalyst gradually moves downward by force of gravity and enters the regenerator located beneath the reactor; at the exit from the reactor steam is blown through the catalyst bed. A blower forces air into the regenerator for burning the coke on the catalyst surface. The combustion products formed during catalyst regeneration are withdrawn from the regenerator. The heat of combustion of the coke can be utilized for producing steam; and there are water pipes located inside the regenerator for this purpose. The regenerated catalyst is moved from the lower part of the regenerator to a bunker by a pneumatic lift, using compressed air supplied by an air blower. The continuous motion of the catalyst results in attrition, the fine particles formed being removed. The catalyst losses are made up for by introducing fresh catalyst.

A dust-form catalyst can be moved through a catalytic reactor from bottom to top by the stream of vapour of the petroleum products subjected to cracking. A schematic diagram of such a unit is given in Fig. 70.

Catalytic-cracking petrols differ from the petrols of thermal cracking in that they contain large amounts of aromatic, naphthenic and isoparaffinic hydrocarbons. Catalytic-cracking petrol is much more stable than the thermal-cracking product. They have octane numbers of 76 to 82 without addition of ethyl fluid. The petrol yield of catalytic cracking, taken with respect to the weight of the raw material, can be as high as 70 per cent. The gases produced contain saturated and unsaturated hydrocarbons from  $C_1$  to  $C_4$ ; the gas yield on the average comprises 12 to 15 per cent of the weight of the raw material.

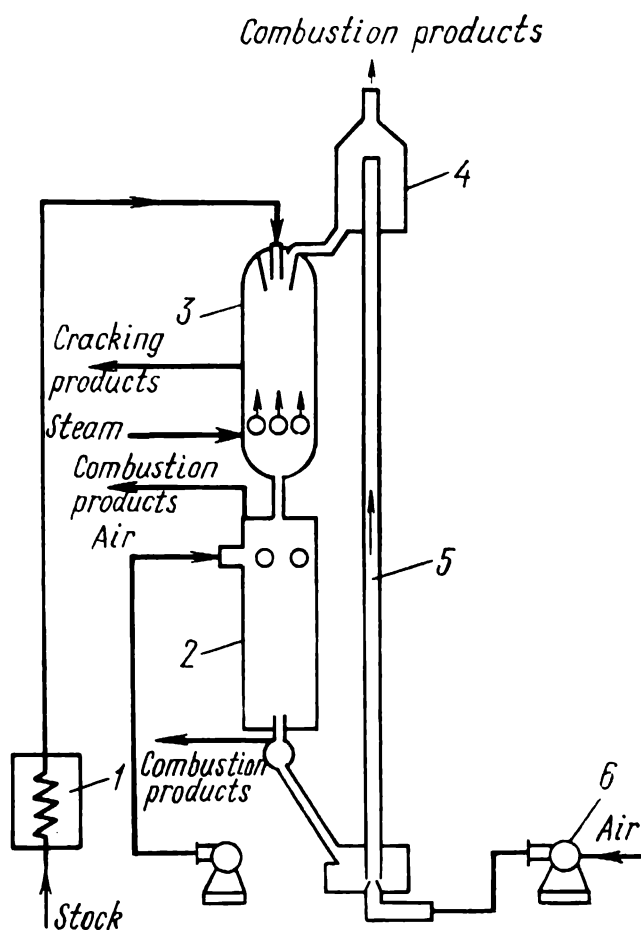


Fig. 70. Schematic diagram of catalytic cracking with a moving catalyst: 1—pipe still; 2—regenerator; 3—catalytic reactor; 4—hopper; 5—pneumatic lift; 6—air blower

The coke deposit on the catalyst can amount to 10 per cent of the weight of the stock. Besides petrol, gases and coke, in the catalytic-cracking process distillates are also formed which are partially recycled to the reactor and circulate through the system.

*Catalytic reforming* is employed more extensively than thermal reforming. Catalytic reforming produces aromatic hydrocarbons by dehydrogenation of six-member naphthenes, dehydrocyclization of paraffins, isomerization of five-member naphthenes into six-member ones, followed by their dehydrogenation and production of aromatic compounds. Simultaneously, hydrocracking reactions and isomerization of paraffinic hydrocarbons also take place. High-octane petrols and such aromatic hydrocarbons as benzene, toluene and xylene can be produced by catalytic reforming.

There are a number of industrial reforming processes in use which differ in the catalyst employed, temperature, pressure, regeneration method, and the state of the catalyst in the process. A common feature is that the reactions are carried out under pressure in an atmosphere of hydrogen to reduce formation of carbon deposits on the catalyst. Most widely used is a so-called platforming process—catalytic reforming of the petrol-ligroine fractions of straight-run distillation, carried out over a platinum catalyst (platinum on aluminium oxide) in the presence of hydrogen. If platforming is carried out at 480-510 °C and at a pressure from 15 to 30 atm, benzene, toluene and xylene are produced. At a pressure of about 50 atm, petrols which have an octane number of approximately 98 without addition of ethyl fluid are produced. Platforming is accompanied by hydrogenation of olefines and sulphur-containing compounds, which form hydrogen sulphide. As a result platforming petrols are distinguished by high stability and low sulphur content.

In all the methods of catalytic reforming, together with liquid products, gases are produced, which contain hydrogen, methane, ethane, propane and butane. The hydrocarbon compounds in reforming gas serve as charging stock for organic and inorganic synthesis of ammonia, methanol and other compounds. The yield of catalytic-reforming gases is 5 to 15 per cent of the weight of the raw material.

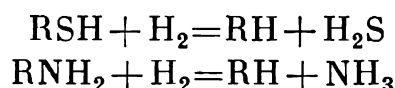
**Purification of the petroleum products.** Petroleum products must be subjected to purification since the products obtained by distillation and cracking contain olefines, diolefines and sulphur-, oxygen- and nitrogen-containing compounds, which cause instability and formation of carbon deposits on the cylinder walls of internal combustion engines, give a dark colour and unpleasant odour to the products, etc. Purification is the final stage in the manufacture of motor fuels and lubricating oils.

Both chemical and physicochemical purification methods are used. The chemical methods include purification with sulphuric acid and

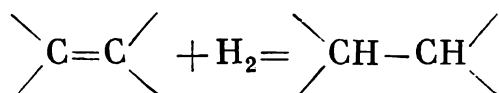
hydrorefining, the physicochemical methods—adsorption and absorption.

Sulphuric-acid purification consists in mixing the product with a small amount of sulphuric acid (90-93 per cent  $\text{H}_2\text{SO}_4$ ) at room temperatures. As a result of chemical reactions a purified product is obtained with the undesirable impurities transformed to the sludge. The sludge is a waste product which can be utilized to make sulphuric acid. Sulphuric-acid purification is cumbersome; large amounts of reagents are consumed, it produces waste products which are difficult to utilize, etc.

In recent years the hydrorefining process has come into wide use. It consists in treating the products being purified with hydrogen in the presence of alumino-cobalt-molybdenum catalysts at 380-420 °C and at a pressure from 35 to 40 atm. In the hydrorefining process hydrogen reacts with sulphur-, nitrogen- and oxygen-containing compounds to form hydrogen sulphide, ammonia and water, which can easily be separated from the material being purified.



The dienes are also hydrogenated, and this increases the stability of the product



Hydrorefining makes it possible to utilize high-sulphur petroleums for producing petroleum products.

Purification by adsorption consists in contacting the products with adsorbents—so-called bleaching clays or silica gel. Sulphurous, oxygen-containing and nitrogenous compounds, asphalts, tars and hydrocarbons, which readily undergo polymerization and must be removed, are adsorbed. Purification by absorption consists in selective solution of undesirable components of the petroleum products. Nitrobenzene, furfural, liquid sulphur dioxide, dichloroethyl ether, etc. are used as selective solvents.

In a number of cases even after purification the petroleum products remain unstable. Stabilization of petroleum products consists in adding very small amounts of antioxidants (inhibitors)—substances which sharply reduce the rate of oxidation of tarry substances, diolefines, etc.—and in this way the petroleum products are made stable for storage. Phenols, aromatic amines, aminophenols, etc. are used as inhibitors.

## 5. Gaseous Fuels

**The composition and properties of the gases.** The gaseous fuels are natural gas, casing-head gas, gas formed in petroleum processing, producer gases, coke-oven gas, blast-furnace gas and others which can

be employed as a fuel or as a raw material for the chemical industry. Such hydrocarbon gases as natural gas, casing-head gas and gases formed in processing petroleum—cracking gas, reforming gas, and pyrolysis gas—are raw materials of very great importance for the chemical industry.

The compositions of natural and casing-head gases vary widely and they depend on the underground conditions, method used for winning the gas, etc. Representative compositions of gases from various fields in the USSR are given in Table 12.

TABLE 12

The Composition of Natural and Casing-Head Gases

Field	Content (% by volume)					
	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>	Higher hydrocarbons	N <sub>2</sub> +CO <sub>2</sub> +H <sub>2</sub> S
<i>Natural gas</i>						
Gazly	94.6	2.20	0.6	0.2	0.4	2.0
Berezovsk	94.75	1.45	0.45	0.05	—	1.42
Shebelinsk	92.5	4.00	1.01	0.31	0.37	1.64
<i>Casing-head gas</i>						
Surakhansk	89.7	0.16	0.13	0.28	1.26	8.4
Buguruslan	72.5	9.8	7.5	8.3	—	1.9
Romashkinsk	37.0	20.0	18.5	8.2	4.7	11.6
Grozny	30.8	7.5	21.5	20.4	19.8	—

The compositions of gases obtained in refining petroleum, which depend on the processing method, are given in Table 13.

TABLE 13

The Composition of Petroleum-Processing Gases

Component	Content (% by volume)			
	Liquid-phase cracking	Pyrolysis	Catalytic cracking	Catalytic reforming
H <sub>2</sub>	3-4	12	5-6	8-10
CH <sub>4</sub>	40-50	55-57	10	4-10
C <sub>2</sub> H <sub>6</sub>	17-18	5-7	3-5	10-15
C <sub>3</sub> H <sub>8</sub>	10-15	0.5	16-20	35-40
C <sub>4</sub> H <sub>10</sub>	5-6	0.2	42-46	30-40
C <sub>2</sub> H <sub>4</sub>	2-3	16-18	3	—
C <sub>3</sub> H <sub>6</sub>	6-8	7-8	6-11	—
C <sub>4</sub> H <sub>8</sub>	4-5	4-5	5-6	—

Besides the products listed in Table 13 the gases contain some heavier gaseous hydrocarbons, among them a pentane-amylene fraction.

Chemical processing of petroleum gases is now carried out by the petrochemical industry, which manufactures a large variety of chemical products—ethyl and methyl alcohols, ammonia, formaldehyde, divinyl, acetic acid, maleic anhydride, various chlorine derivatives used in making polymer materials, fertilizers, etc. The cost of various products made from hydrocarbon gases is considerably lower than that of the products made from other kinds of raw materials.

**Processing the hydrocarbon gases.** The hydrocarbon gases, as can be seen from Tables 12 and 13, are very complex mixtures. The raw material for making a chemical product must in most cases be a very narrow fraction of a hydrocarbon mixture or an individual hydrocarbon. For this reason, prior to chemical processing the raw material is subjected to pretreatment, the most important operation being separation of the gases into narrow fractions or individual hydrocarbons. The following methods of separating gas mixtures are in commercial use: compression (condensation), absorption-desorption, adsorption-desorption, low-temperature condensation and distillation.

The method used for chemical treatment of hydrocarbons depends on their properties. The principal methods employed are pyrolysis, catalytic dehydrogenation, oxidation, hydrogenation, hydration, conversion, halogenation, nitration, alkylation, isomerization, and polymerization; they are used in making ethylene, propylene, butane, acetylene, aldehydes, alcohols, acids, ketones, halogen- and nitro-derivatives, polymers, etc. Alkylation, isomerization and polymerization of hydrocarbons are utilized for making high-octane components of fuels.

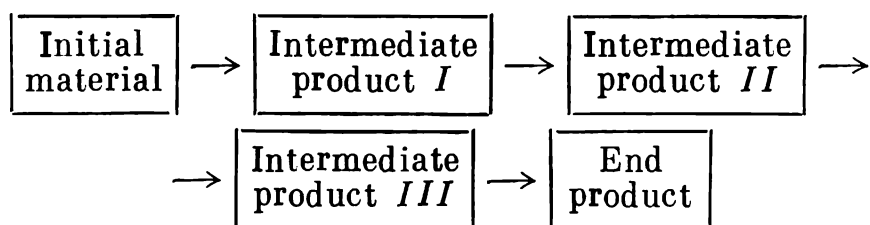
The amounts and the variety of organic-synthesis products made by the chemical industry continue to grow from year to year. These products include various monomers and the synthetic resins, rubber, fibres, plastics, adhesives, dyes, a large number of different paints and varnishes, lubricants, solvents, surface-active agents, insecticides, flotation chemicals, antifreeze- and antiknock agents, explosives, pharmaceuticals, photochemicals, perfumes, etc., made from them.

### 1. The Raw Materials for Industrial Organic Synthesis

The substances involved in the manufacture of complex organic compounds are divided into raw, or initial, materials, intermediate products and end products.

**The initial materials**—methane, ethylene, propylene, butylene, acetylene, benzene, toluene and other individual hydrocarbons are the most important of the substances used in organic synthesis; they are obtained by the chemical processing of gaseous, liquid and solid fuels. At one time the principal source of the raw materials for organic synthesis was the coal tar obtained in coking and low-temperature carbonization. Raw materials of plant and animal origin were also extensively employed. In more recent times liquid hydrocarbons contained in petroleum, natural gas and casing-head gases, and also the gases formed in processing petroleum have become predominant. At present many of these initial materials are produced in amounts of tens and hundreds of thousands of tons per year.

**Intermediate products**—ethylene oxide, acetaldehyde, phenol, nitrobenzene and others—are obtained by processing the initial materials and they are themselves materials used in making more complex organic compounds (plastics, fibres, dyes, pharmaceuticals, physiologically active agents, etc.). The ties between the initial raw material and the end product can be represented by the following scheme:



They are illustrated by the following example.

Benzene—a product of the petrochemical and coke-benzene industries—is an excellent solvent for fats, resins, rubbers, sulphur and other compounds. It is also an initial material used in making nitrobenzene, aniline, chlorobenzene, phenol, ethyl benzene, isopropylbenzene, styrene, DDT, maleic anhydride, phenylethyl alcohol, monosulphonic acid and other chemical products and intermediate products employed in manufacturing dyes, synthetic rubber, plastics, varnishes, insecticides, pharmaceuticals and disinfectants, explosives, etc.

The product made by oxidation of ethylene—ethylene oxide—is employed for manufacturing ethanamine, ethyleneglycol, di- and polyethyleneglycol, acetic aldehyde, dioxane, ethylene chlorohydrin, styrene, ethylene cyanohydrin and from them—synthetic resins, synthetic rubber, plastics, varnishes, fibres, detergents, antifreeze, and other industrial items.

At the present time the organic-synthesis industry employs the following principal kinds of raw materials: natural gas and casing-head gas; gaseous and liquid hydrocarbons obtained by distillation of petroleum and by cracking and pyrolysis of petroleum products; solid paraffinic hydrocarbons and heavy petroleum residues, coke-oven and shale gases, coal tar and tars obtained from shale, wood and peat.

How petroleum raw materials are used for making diverse products is shown in Fig. 71. Besides these, in organic technology a large number of inorganic compounds are also employed: acids, alkalies, soda ash, chlorine, etc., without which many of the processes cannot be carried out.

As a rule, all raw materials must be subjected to purification to remove water vapour, mechanical admixtures, sulphurous compounds and other impurities, and then be separated to obtain individual hydrocarbons. In other words, a purified raw material must first be obtained, which can then be processed into semiproducts and pure products.

The methods used to separate the gaseous hydrocarbons include compression under cooling, absorption-desorption and adsorption-desorption (see Part I). Liquids are usually separated by distillation and rectification. Very often in industrial processing a combination of two or more of the methods named is employed.

These methods of separating raw materials and modern processing methods are employed to obtain the most important of the intermediate products, which serve as the direct starting materials for organic synthesis: synthesis gas (a mixture of  $H_2$  and  $CO$ ); saturated, aliphatic hydrocarbons (from methane to pentanes); individual monoolefines ( $C_2$  and higher) and their mixtures, diolefines—butadiene, isoprene, etc.; acetylene; aromatic hydrocarbons—benzene, toluene, xylene, etc.



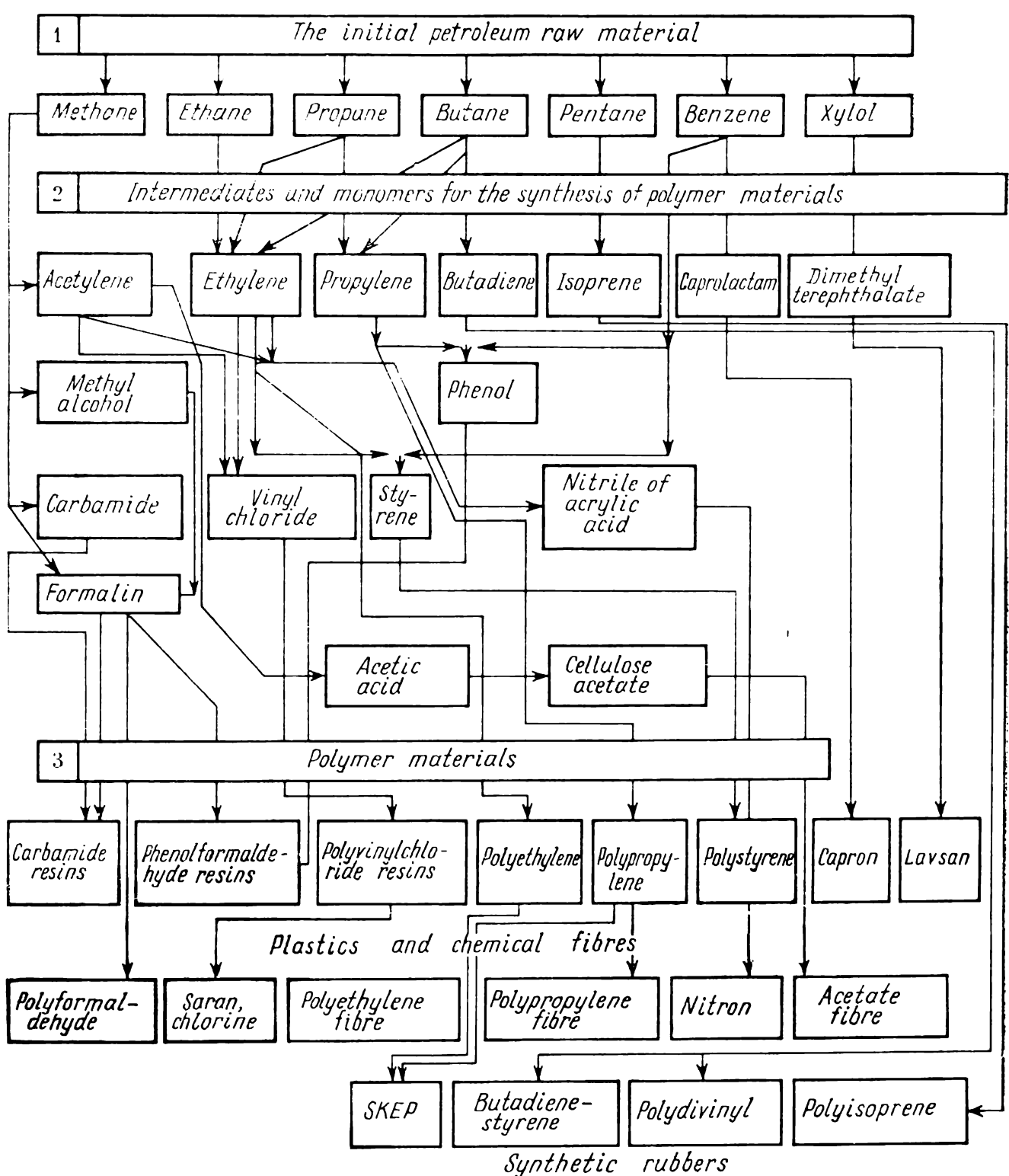


Fig. 71. How petroleum products are employed as raw materials in industrial organic synthesis

## 2. Processes Employed in Industrial Organic Synthesis

The methods employed for processing any raw material depend on the nature of the product to be obtained from it and also on the composition and properties of the initial hydrocarbons. Typical organic-chemistry processes are used for making organic-synthesis products: halogenation, sulphonation, oxidation and reduction, hydrogenation and dehydrogenation, hydration and dehydration,

nitration, alkylation, cyclization, isomerization, condensation, polymerization, esterification etc. The organic chemical industry is based mainly on synthesis reactions, i.e. on obtaining complex compounds from simple ones; however, decomposition reactions are also employed. The classification of organic-synthesis processes and basing their nomenclature on the type of reaction used is rational since most of the processes of organic synthesis are kinetics controlled, i.e. the overall rate of the process,  $u$ , depends on the rate of chemical reactions and is described by the equation:

$$u = \frac{dG}{d\tau} = kv \Delta C \quad (9.1)$$

or

$$u = \frac{dx}{d\tau} = k \Delta C \quad (9.2)$$

in which the driving force of the process  $\Delta C$  is equal to the product of the concentrations of the reagents in accordance with the kinetics equation, which determines the reaction order, and the rate constant is governed by the Arrhenius equation.

In organic-synthesis processes usually not one, but a number of parallel and consecutive reactions occur. As a result, along with the desired product, different coproducts and waste products are formed. The rate constant of the overall process,  $k$ , may therefore be a complex function of the rate constants of the separate reactions:

$$k = f(k_1, k_2, k_3, k_4, \dots) \quad (9.3)$$

and the functional relationship may change very sharply with the temperature, pressure and concentrations of the reacting components and other regime variables. The selectivity of a process with respect to the desired product is given by the ratio of the rate constant of the principal reaction to that of the side reactions (see Part I, Chapters 3 and 6). In accordance with this, a commonly used means for intensifying the processes of organic synthesis is to employ selective catalysts which only accelerate the main reaction. Polymerization, hydrogenation and other processes resulting in a decrease in volume are often carried out at medium or high pressures to accelerate the process and to increase the equilibrium yield. Gas-absorption processes, which are frequently encountered in organic synthesis, can be carried out with advantage at high pressures. The inverse processes of desorption, dehydrogenation, splitting of molecules to produce gaseous products should be carried out under vacuum.

In gas-phase reactions of oxidation, chlorination, hydrogenation, etc. the process driving force  $\Delta C$  and rate  $u$  are increased by varying the temperature and pressure, so as to shift the equilibrium towards maximum formation of the end product. When using sorption techniques, the process driving force is increased by raising the concentra-

tion of the reacting components or removing the end product from the reaction zone.

Utilization of various means for intensifying production processes is often limited by low stability of the organic compounds. This is especially so with respect to high temperatures (due to decomposition of the molecules of the starting materials and the products).

Not only catalysts, but also initiators, and photosynthesis and irradiation techniques are used to increase the rate constant in making organic intermediates. Oxidation of paraffinic hydrocarbons, chlorination of benzene, polymerization of ethylene, the manufacture of graft-polymers, vulcanization of rubber, etc. can be carried out using ionizing radiation. In many cases the products formed are better than those obtained in ordinary ways. Thus, following irradiation, sulphochlorinated polyethylene possesses higher heat resistance and also resistance to acids and strong oxidizing agents, including ozone. A significant advantage of radiation-chemical reactions is a marked reduction of the induction period, and in some cases its complete absence.

For accelerating heterogeneous processes which are diffusion-controlled (see Part I, Chapter 2), intensive agitation of the phases is used to replace molecular diffusion by convective diffusion and reduce the diffusion resistance, which slows interaction between the reaction components.

Whether or not a given method should be used for intensifying a process depends on economic factors particularly on the need to use complex equipment. Development of new production schemas and new processes has been accompanied by continuous improvements in the design of equipment. New, improved apparatus provides a continuous process throughout the complete chain of manufacturing operations and integral utilization of raw materials. Modern organic-synthesis plants are made up of a combination of various production sections; not only is a given (basic) product made, but also most of the coproducts, formerly waste products, are recovered and processed.

Processes of organic synthesis have had a great effect on the technology of petroleum-processing plants; there has been very strong intertwining of fuel and chemical processing. Since the organic-synthesis manufacturing processes are so manifold and varied, only some of the most typical and economically important are discussed below.

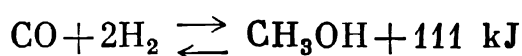
### 3. The Manufacture of Methyl Alcohol

Methyl alcohol (methanol) is an important raw material for manufacturing mainly formaldehyde, and also dimethyl sulphate, dimethyl terephthalate, methyl acetate, dimethyl formamide, antiknock-mixtures (tetramethyl lead), inhibitors, antifreeze, methyl-

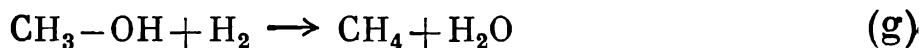
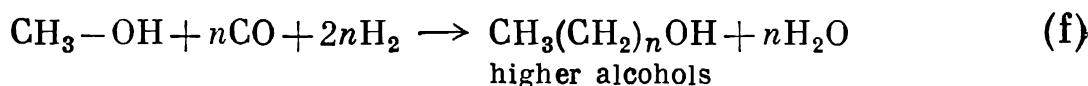
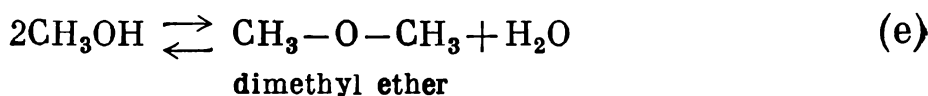
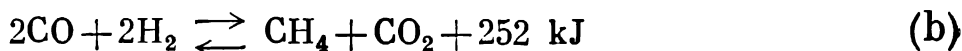
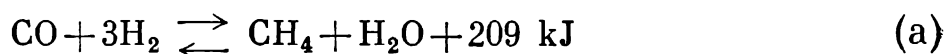
amine, the methyl ester of acrylic acid, varnishes, dyes, and other products. The pur eproduct is used as a solvent and can be employed as a high-octane admixture to motor fuels.

The synthesis of methyl alcohol is similar to ammonia synthesis, both with respect to the physicochemical conditions of the process and the technology. Synthesis gas can be produced in the same fashion as the nitrogen-hydrogen mixture by conversion of producer gas or natural gas. In both processes mixtures of carefully purified gases react at high pressure and temperature in the presence of a catalyst. Finally, due to the low yield of the end products, both processes employ continuous recycling and the reaction never proceeds to complete conversion. Due to this similarity analogous apparatus is employed in both these synthesis processes, often both are carried out at one and the same plant.

In this synthesis a gas mixture with a CO : H<sub>2</sub> ratio of 1 : 4 to 1 : 8 is used. The process is carried out at 350-400 °C and a pressure of 200-300 atm in the presence of a mixed zinc-chromium catalyst (ZnO + Cr<sub>2</sub>O<sub>3</sub>). The basic reaction of the process is



Simultaneously, especially if the pressure is below or the temperature above the optimum values, the following side reactions can occur:



The amount of a given side-product present in the reaction mixture depends not only on the temperature and pressure, but also on the other regime variables, such as the composition of the initial gas mixture, the selectivity and the physical condition of the catalyst. Methane is as a rule the most significant admixture. However, formation of methyl alcohol results in maximum decrease in volume, as compared to the side reactions (a)-(g), and according to Le Chatelier's rule, increased pressure results in a shift of the equilibrium towards the formation of methyl alcohol. Since the process is exothermic,

if the temperature is increased, the equilibrium shifts to the left, and the degree of conversion of synthesis gas to methanol is reduced. However, if the temperature is not high enough, the process rate will be extremely slow. Because of this the commercial process is carried out within a narrow temperature range with fluctuations not exceeding 20-30 °C.

The equilibrium constant of the basic reactions

$$K_p = \frac{P_{\text{CH}_3\text{OH}}}{P_{\text{CO}} \cdot P_{\text{H}_2}^2}$$

can be computed using the following equation:

$$\log K_p = 3970 T^{-1} - 7.49 \log T + 0.00177T - 0.0731 T^2 + 9.22 \quad (9.4)$$

The equilibrium concentrations of methanol at temperatures of 300 and 350 °C for pressures from 50 to 400 atm for an initial mixture containing 33.3 % CO and 66.7 % H<sub>2</sub> are listed in Table 14.

TABLE 14

Methanol Concentration at Equilibrium  
as a Function of Pressure

Pressure, atm	Equilibrium methanol concentration (%) at the temperature of	
	300 °C	350 °C
50	9.9	—
100	26.3	8.2
200	53.4	24.0
300	76.0	37.7
400	86.0	53.1

Due to insufficient activity and selectivity of the catalyst employed the actual yield is always below the equilibrium value.

Many metals exhibit catalytic properties for the methanol-synthesis reaction. In industry a zinc-chromium catalyst is employed, which is made by precipitating oxides of zinc and chromium in a ratio of ZnO : Cr<sub>2</sub>O<sub>3</sub> ≈ 2 : 1. The catalyst is reduced in a stream of the synthesis gas. The period during which the catalyst operates continuously without regeneration is from 4 to 6 months.

Studies of synthesis of methanol over a zinc-chromium catalyst in a fluidized bed in a wide range of the regime variables (300-400 °C, 50-250 atm, at very high space velocities of from 358 000 to 800 000 hr<sup>-1</sup>, H<sub>2</sub> : CO = 2.6 : 8, mean diameter of the catalyst pellets 0.38-2.5 mm) showed that Temkin's equation can be employed to describe the process rate. It was found that the overall rate of the

synthesis reaction depends on hydrogen adsorption. From the experimental data the values of the exponents of the component concentration terms were obtained and the equation for the reaction kinetics was found to be:

$$u = \frac{dx}{d\tau} = k_1 \frac{p_{H_2} p_{CO}^{0.25}}{p_{CH_3OH}^{0.25}} - k_2 \frac{p_{CH_3OH}^{0.25}}{p_{CO}^{0.25}} \quad (9.5)$$

where  $k_1$  and  $k_2$  are the rate constants of the forward and reverse reactions. The dependence of the rate constant of the forward reaction on

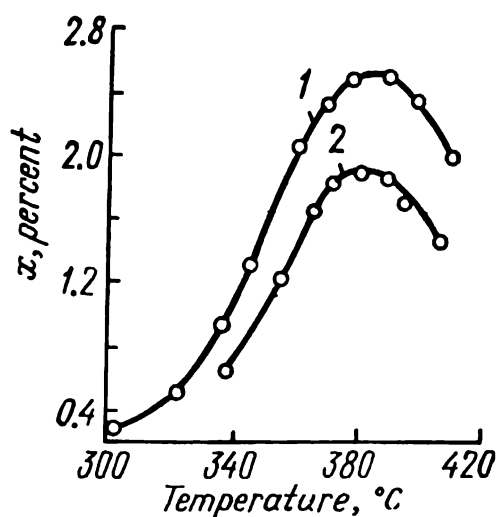


Fig. 72. Methanol yield vs reaction temperature for a mean catalyst-pellet size of 0.38 mm,  $P = 250$  atm,  $H_2 : CO = 8$ ,  $V_{space} = 450\,000$  hr<sup>-1</sup>:

1—crude alcohol; 2—pure alcohol

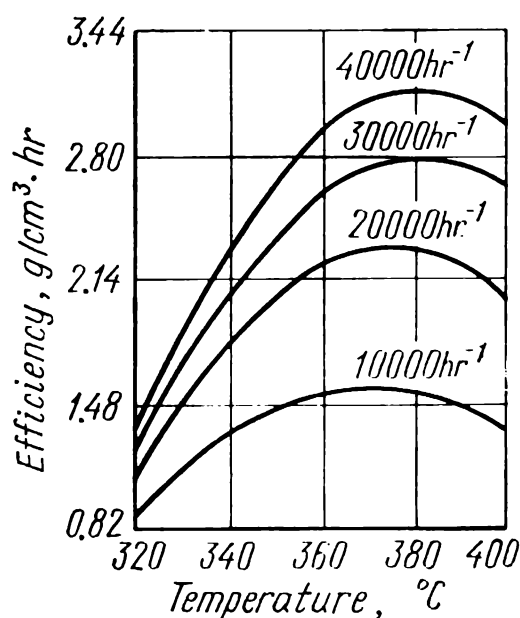


Fig. 73. Dependence of catalyst efficiency at 300 atm on space velocity

the temperature is described by the Arrhenius equation and corresponds to an activation energy of  $E = 100$  kJ/mole.

The interval of optimal temperatures, at which the yield of the product is largest, depends on the catalyst activity, the space velocity of the gas mixture, and the pressure. For a zinc-chromium catalyst at pressures of 50 to 250 atm and space velocities of 20 000–40 000 hr<sup>-1</sup> the optimal temperatures lie between 360 and 380 °C. Over a low-temperature catalyst, for example, a copper-zinc-aluminium catalyst, which operates at 220–280 °C, the process is carried out under a lower pressure of 40 to 100 atm. In Fig. 72 curves are given showing the total and the useful conversion of CO, expressed in per cent of the initial carbon monoxide.

In industrial conditions synthesis is carried out at space velocities of 20 000–40 000 hr<sup>-1</sup> and the yield of methanol obtained in a single pass of the mixture through the catalyst is about 4 per cent. If the

space velocity is increased to  $100\,000\text{ hr}^{-1}$  conversion of the initial mixture for one pass is reduced, but if a recycle scheme is used the amount of methyl alcohol produced rises since the drop in the degree of conversion is lower than the increase in the space velocity (Fig. 73). The methanol yield as a function of the space velocity of the reacting gases for  $370^\circ\text{C}$  and  $250\text{ atm}$ , over a zinc-chromium catalyst is given below.

Space velocity of the gas, $\text{hr}^{-1}$	Methyl-alcohol yield, $\text{g/l}\cdot\text{hr}$
2 400	170
9 000	327
18 000	375
35 000	750

Industrially, synthesis of methanol is carried out according to the flow diagram of Fig. 74. The initial gas mixture, after preliminary

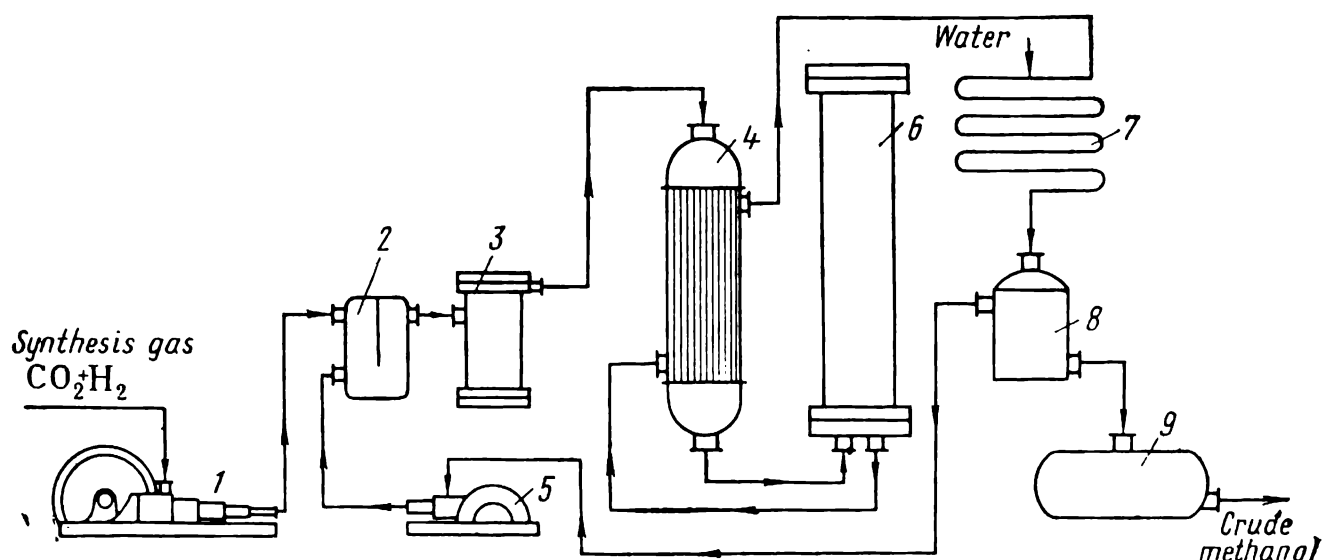


Fig. 74. Flow diagram of methyl alcohol synthesis from carbon monoxide and hydrogen:

1—compressor; 2—mixer; 3—filter; 4—shell-and-tube heat exchanger; 5—recirculation compressor; 6—synthesis tower; 7—cooler-condenser; 8—separator; 9—crude-alcohol tank

removal of impurities from it, is compressed in a five-stage compressor to  $250\text{ atm}$ . A cooler (not shown in the diagram) removes the heat of compression after each stage. Fresh gas is then mixed with recycled gas in a mixer and after passing through a filter for removing oil it enters into the tubes of a heat exchanger, where it is heated to approximately  $220^\circ\text{C}$  by the gases leaving the reactor, after which it is directed to the synthesis tower (height  $12\text{--}18\text{ m}$ , inner diameter  $0.8\text{--}1.2\text{ m}$ , and wall thickness  $0.09\text{--}0.1\text{ m}$ ). The necessary temperature is maintained in the tower by utilizing the heat of the reaction, part of it being taken up by the gas mixture flowing through the heat-

exchanger tubes on its way to the catalyst zone. If necessary, cold gas-mixture is introduced into the tower to control the temperature.

Synthesis towers differ in the type of packing employed. In shelf-type towers the catalyst is located in several beds and the gas consecutively passes through each bed. Fig. 75 is a diagram of a methanol-synthesis tower in which the catalyst basket, electric heater and heat exchanger are all contained in a single body. The synthesis gas enters at the top and passes down through the annular space between the tower body and the catalyst basket. Then the gas flows through the intertube space of the heat exchanger, where its temperature is raised by removing heat from the synthesis gases flowing inside the heat-exchanger tubes. Heat exchange is better in towers of this type and this results in a closer approach to an isothermic process. The tower operates under close to plug-flow conditions.

The contact gases leave the tower at the bottom and after giving up heat to the initial gas mixture in the heat exchanger they flow through a water cooler-condenser to a separator. Here the crude alcohol produced (96 per cent concentration) is separated from the unreacted gases, which are compressed by a recycle compressor to the pressure of the initial gas and are transferred to the mixer, whereas the methyl alcohol is sent to the crude-alcohol tank.

Since the impurities and products of various side reactions (methane, nitrogen, carbon dioxide, etc.) accumulate in the circulating gas mixture, it is periodically brought up to standard by burning part of the recycle gas. Approximately 700 m<sup>3</sup> of CO and 1400-2000 m<sup>3</sup> of H<sub>2</sub> are consumed to produce 1 ton of methyl alcohol (about 400 g of alcohol is formed per cubic

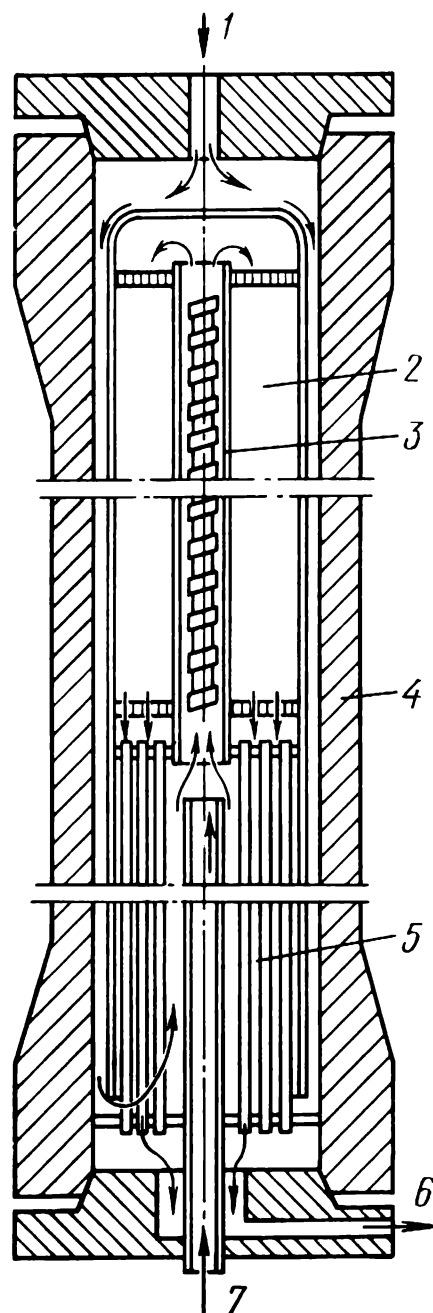


Fig. 75. Schematic diagram of a methanol-synthesis tower:

1—main gas stream; 2—catalyst basket; 3—electric heater; 4—tower body; 5—heat exchanger; 6—gas exit; 7—by-pass gas



metre of synthesis gas, i.e. the yield lies between 84% and 87% of the theoretical value).

Carbon monoxide reacts with carbon steel to form iron pentacarbonyl,  $\text{Fe}(\text{CO})_5$ , which decomposes on the surface of the catalyst and covers it with a layer of dispersed iron; this accelerates side reactions resulting in formation of methane, which in turn results in deviations from the optimal temperature regime. To prevent carbonyl corrosion the tower walls and some of the tower parts are covered with copper or are made of high-alloy steel.

The crude methanol produced is purified to remove acids, esters, higher alcohols and iron pentacarbonyl, which, together with distillation which follows, yields pure methyl alcohol.

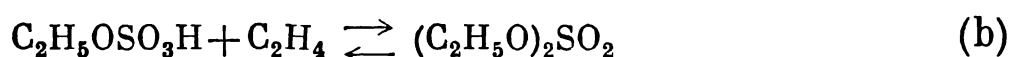
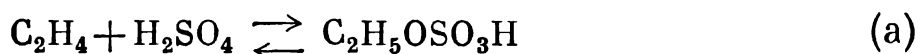
There is an electric heater inside the synthesis tower for heating the gas mixture in the starting-up period. By changing the conditions of synthesis—the temperature, pressure, CO-to- $\text{H}_2$  ratio of the initial gas mixture, and catalyst composition, not only methyl alcohol, but also higher alcohols, aldehydes, ketones, esters, organic acids, saturated and unsaturated hydrocarbons with any desired chain length up to that of solid paraffins, but primarily with unbranched structures, can be obtained. The initial gas mixture must be carefully purified to remove harmful impurities—sulphurous compounds, tars and dust.

#### 4. The Manufacture of Ethyl Alcohol

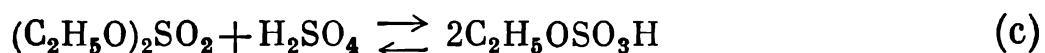
Ethylene  $\text{CH}_2=\text{CH}_2$ , propylene  $\text{CH}_3-\text{CH}=\text{CH}_2$ , butylene  $\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2$ , butadiene (divinyl)  $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ , all of which are highly reactive compounds, are very important in industrial organic synthesis. Of the manifold reactions into which olefines enter, the most important industrially are polymerization (polyethylene, polypropylene, polyisobutylene, etc.), hydration (alcohols), chlorination (dichloroethane, allyl chloride, etc.), oxidation (ethylene oxide), oxo-synthesis and some others. Processes in which olefine hydrocarbons are hydrated are now extensively used. Ethyl-, isopropyl- and other alcohols are manufactured in this way. At present more ethyl alcohol is produced than any other organic product. From year to year the production of alcohol from food-product raw materials is being replaced by its production through synthesis, hydrolysis and the sulphite process (see page 258); one ton of ethylene is equivalent to 4 tons of grain. Synthetic alcohol made from ethylene costs several times less than that made from food-products and less labour is involved in its production. Synthetic alcohol is widely used in various branches of industry: for making synthetic rubber, celluloid, acetaldehyde, acetic acid, artificial silk, pharmaceuticals, perfumes, cordite, as a solvent, etc.

*Hydration of ethylene* can be carried out by two methods: using sulphuric acid (sulphuric-acid hydration) and by the forward reac-

lion of ethylene with steam over a solid catalyst (vapour-phase catalytic hydration). The sulphuric-acid method was proposed by A. M. Butlerov, but the industrial process was developed only in the post-war years. It consists of four operations: (1) absorption of ethylene with sulphuric acid to produce methyl sulphate; (2) hydrolysis of the esters; (3) separation of the alcohol and its rectification; (4) concentration of the sulphuric acid. Interaction between ethylene and sulphuric acid occurs in two stages: the first is physical dissolution of the ethylene in the acid, and the second the homogeneous reaction of both components to form alkylsulphates according to the equations



Under the conditions in which the process is carried out, diethyl sulphate can react with sulphuric acid to form ethyl sulphate:



Sulphuric acid absorbs ethylene at a lower rate than other gaseous olefins (for example, hundreds of times slower than isobutylene). As ethylsulphuric acid (ethyl sulphate), in which ethylene is dissolved better, is formed, the rate of absorption of ethylene increases. However, since, simultaneously, the concentration of sulphuric acid decreases, the overall process rate is also reduced. The required concentration of 0.6 mole  $\text{C}_2\text{H}_4$  per mole  $\text{H}_2\text{SO}_4$  in the upper part of the absorber is achieved with 97.5 per cent acid in 1 hr 15 min, i.e. almost twice as rapid as with 95 per cent  $\text{H}_2\text{SO}_4$  (2 hr 15 min). Consequently, it is best to use 97-98 per cent acid. The optimal temperature for the process is 65-75 °C. If the temperature is raised still higher the amount of ethylsulphuric acid formed drops.

The effect of the pressure on ethylene absorption is shown in Fig. 76. When the pressure is raised the rate of absorption and the degree of saturation of the sulphuric acid with ethylene grows. Intensive agitation is very important for the process. Bubble-type towers are used, since they provide better agitation than that obtained

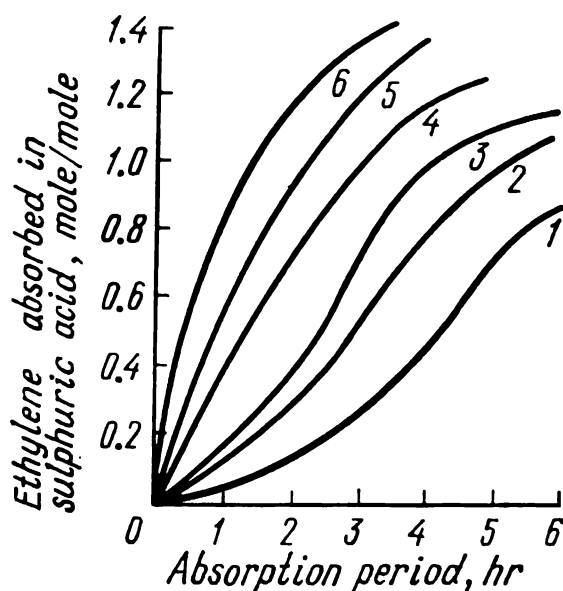
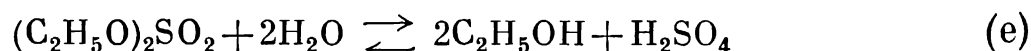
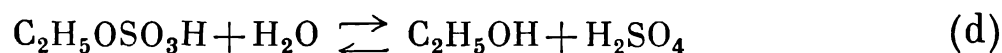


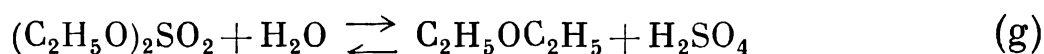
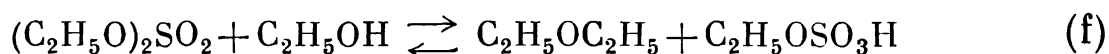
Fig. 76. Dependence of degree of ethylene absorption by sulphuric acid on the pressure:

1—1.9 atm; 2—3.1 atm; 3—7.6 atm; 4—10 atm; 5—16.5 atm; 6—23.6 atm

in packed towers. In the second stage ethyl- and diethyl sulphates are hydrolysed by the reactions:



Along with the principal reactions, (d) and (e) formation of diethyl ether also takes place:



and also formation of acetaldehyde and polymerization of ethylene. To lower the amount of diethyl ether produced, hydrolysis is carried

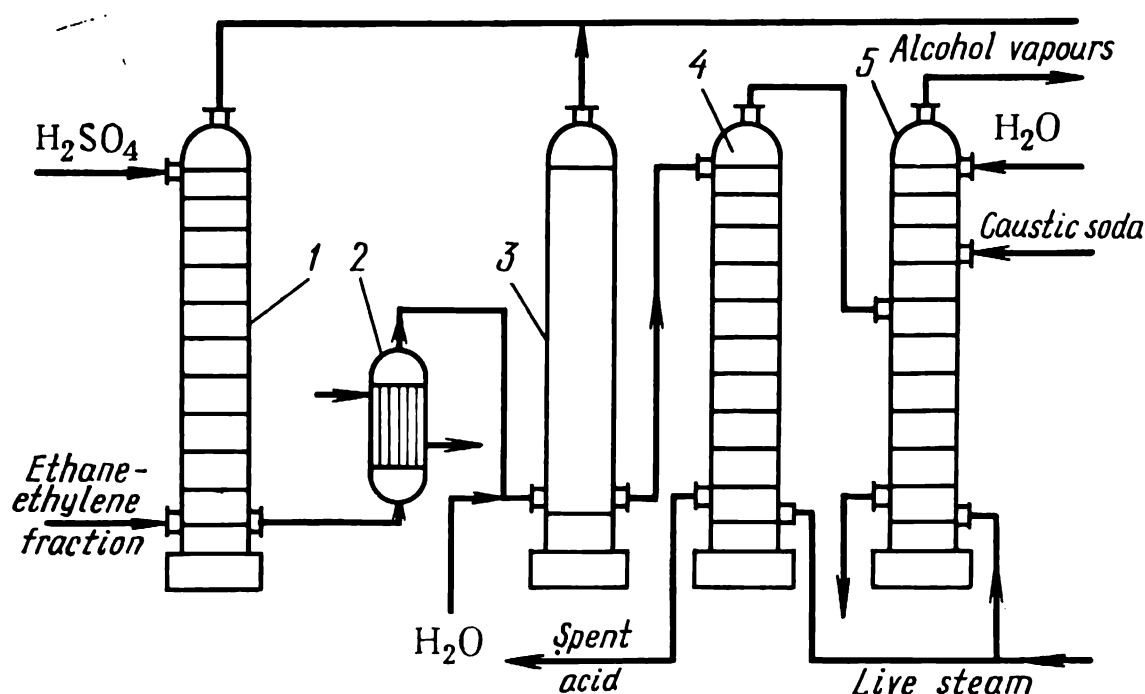


Fig. 77. Flow diagram of process for manufacturing ethyl alcohol by sulphuric-acid ethylene hydration:

1—absorber; 2—heat exchanger; 3—hydrolyzer; 4—stripping tower; 5—neutralization tower

out at the maximum possible rate; the alcohol formed is immediately stripped from the solution, so as to keep its concentration very low.

The principal process flow diagram used for manufacturing ethyl alcohol by sulphuric-acid hydration of ethylene is given in Fig. 77. The ethylene-ethane fraction obtained in processing petroleum, which contains 60-75 per cent ethylene, is fed at a pressure of 20-25 atm to the bottom of a plate-type absorber (approximately 20 bubble-cap plates) lined with acid-resistant tiles and bubbles up through the layer of acid on each plate. Concentrated acid (97-98 per cent  $\text{H}_2\text{SO}_4$ ) is introduced at the top of the absorber. When ethylene is absorbed with sulphuric acid large amounts of heat are liberated (121 kJ per

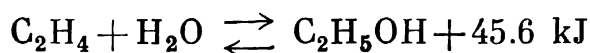
mole of ethylene absorbed) and it is continuously removed by water coolers located on each of the plates, so as to maintain the temperature in the absorber below 80 °C.

The remaining unabsorbed gases (mainly ethane and other impurities, with no more than 2-5 per cent ethylene) are washed with water and then a 10 per cent alkali solution in gas scrubbers. The sulphuric acid solution goes from the absorber to a hydrolyzer with a ceramic packing where it is diluted with water (to a concentration of 50 per cent  $\text{H}_2\text{SO}_4$ ). The temperature in the hydrolyzer is maintained at 100-110 °C and the pressure at 2-3 atm. Hydrolysis lasts 30 min.

The liberated gases, which contain small amounts of diethyl-ether vapours, are removed at the top of the hydrolyzer, washed and neutralized. The solution leaving the hydrolyzer contains ethyl alcohol, water, sulphuric acid (with a concentration of 43-50 per cent), diethyl ether, dissolved gases and unhydrolyzed ethyl sulphates. The mixture next goes to a stripping tower (1.5 atm, 95-125 °C), where final hydrolysis takes place. The gas-vapour mixture leaving the tower is washed, neutralized and the vapour is condensed. The crude alcohol obtained is then subjected to distillation.

The weak sulphuric acid is subjected to purification for removing tarry impurities, and after concentration is again fed to the absorber. For producing one ton of alcohol two tons of concentrated sulphuric acid must be fed to the absorber, i.e. four tons of weak acid must be concentrated by evaporation. This acid recycle makes the process very complex due to corrosion and difficult working conditions. The sulphuric-acid method yields 1.2 tons of crude alcohol and about 100 kg of ethyl ether per ton of ethylene processed. About 90 per cent of the ethylene feed is converted into alcohol.

At present an improved method, vapour-phase catalytic hydration with a recycle flow scheme is continually growing in popularity. Hydration is an exothermic, reversible reaction:



The value of the reaction equilibrium constant can be computed from the equation

$$K_p = \frac{2100}{T} - 6.195 \quad (9.6)$$

It follows from the equation and the thermodynamic data of Fig. 78 that to shift the equilibrium towards hydration of ethylene, the temperature must be lowered and the pressure increased; however at temperatures below 280 °C the hydration rate is very low and the use of pressures above 80 atm is uneconomical.

Phosphoric acid deposited on a large-pore carrier—kieselguhr, silica gel or aluminosilicate—is employed as the catalyst. The use of a carrier with large pores results in an increased rate of diffusion.

Since in this case, acidic heterogeneous catalysis is effected by free acid in the liquid state on the surface of the carrier (a water-absorbing film) the activity of the catalyst depends on the acid concentration, which in turn depends on the partial water-vapour pressure (Fig. 79). Thus, at a water-vapour pressure of 27.5 atm the acid has a concentration of 83 per cent at 280 °C and 85 per cent at 290 °C.

In wide-scale laboratory investigations and tests of industrial units it was found that the values of the fundamental process variables of

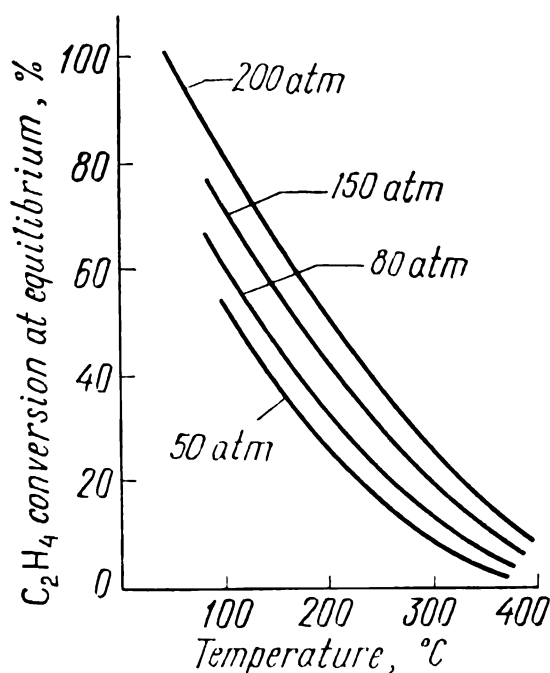


Fig. 78. The dependence of conversion of ethylene to alcohol at equilibrium on temperature and pressure

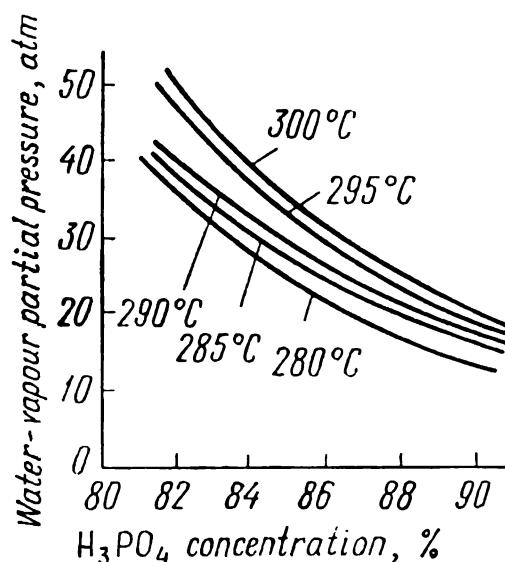


Fig. 79. Water-vapour partial pressure vs phosphoric-acid concentration at various temperatures

the reaction between gaseous ethylene and water vapour should be: (1) a temperature of 280-290 °C, (2) pressure of 70-80 atm, (3) ethylene concentration in the recycle gas of 80-85 per cent by volume, (4) molar ratio of water to ethylene of 0.6 : 1-0.75 : 1, (5) phosphoric-acid concentration on the catalyst surface not under 83 per cent, and (6) a space velocity of 1800-2500 hr<sup>-1</sup>.

These conditions yield a water-alcohol solution containing 15-16 per cent alcohol with 4 to 5 per cent ethylene-conversion in one passage. Overall, useful consumption of ethylene amounts to 95 per cent. The remaining 5 per cent of the ethylene is converted into: diethyl ether (2 per cent), acetaldehyde (1 per cent), dimers and polymers (2 per cent).

The direct ethylene-hydration process (Fig. 80) consists of several continuous operations: (1) preparation of the initial vapour-gas mixture, (2) ethylene hydration, (3) neutralization of the vapours of the reaction products, (4) recuperation of the heat of the recycle streams and (5) purification of the recycle gas. Hydration of ethylene is car-

ried out in a catalytic reactor lined with copper to protect it against corrosion.

Ethylene compressed with a compressor is mixed with water vapour and the mixture is passed through a heat exchanger to the furnace, from which at a temperature of  $280^{\circ}\text{C}$  it enters into a hydrator containing a solid catalyst in a bed 8.5 m high. The residence time in the reactor is from 18 to 20 seconds. The temperature of the initial mixture necessary for the process can also be obtained by direct

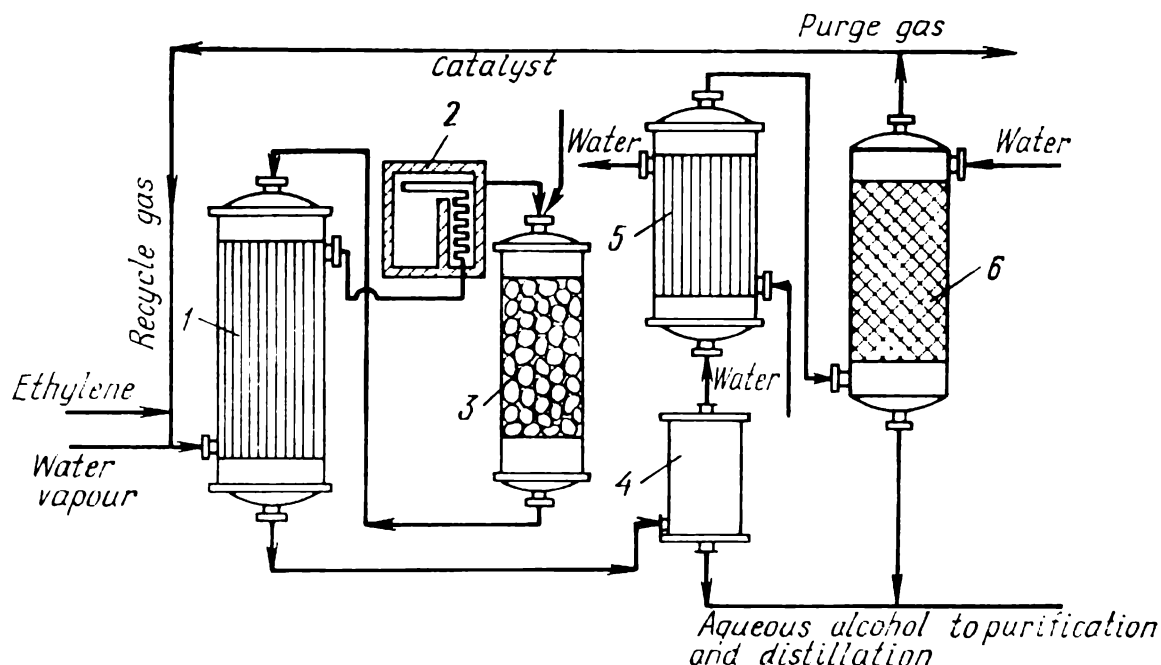


Fig. 80. Flow diagram of process for manufacturing ethyl alcohol by catalytic hydration of ethylene in the vapour phase:

1—shell-and-tube heat exchanger; 2—furnace; 3—reactor; 4—tank; 5—cooler; 6—packed scrubbing tower

mixing of ethylene and superheated steam at a high pressure (about 70 atm). The hydrator corresponds approximately to a model of an adiabatic reactor with ideal plug flow.

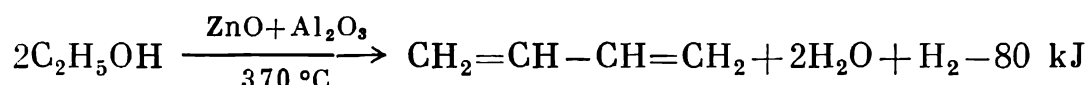
The mixture produced by the reaction is first cooled in a heat exchanger where an aqueous alcohol solution is formed, which is collected in a tank and is finally cooled in a cooler. Full recovery of the alcohol vapour from the gas is achieved by scrubbing it in a tower. The unreacted ethylene is compressed and recycled to the hydrator; the crude alcohol is subjected to distillation. Approximately 0.685 t ethylene, 5.6 kg phosphoric acid, 2 kg of the carrier and 16 kg caustic soda are consumed per ton ethanol made. The service time of the catalyst may be as long as 600 hr. By spraying pulverized phosphoric acid into the reactor during the course of the process the service time of the catalyst can be increased, after which it must be replaced because its surface becomes covered with tarry compounds.

Vapour-phase catalytic hydration of ethylene has advantages over the sulphuric-acid process.

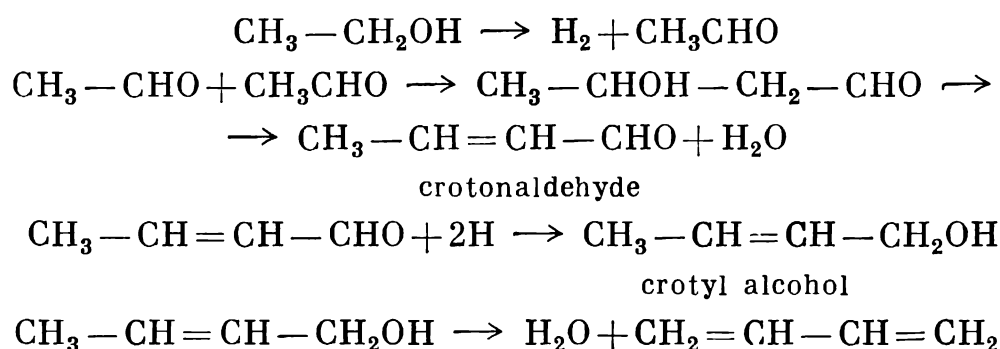
### 5. The Manufacture of Butadiene-1,3 (Divinyl)

Compounds with conjugate double bonds—divinyl (butadiene-1,3), isoprene, chloroprene—and those with a single double bond—isobutylene, styrene,  $\alpha$ -methylstyrene, acrylonitrile, etc.—are used in manufacturing synthetic rubbers. Most of these compounds are obtained by dehydration of the corresponding hydrocarbons, which are contained in industrial petroleum gases, casing-head gases, natural gasoline and some fractions of petroleum-processing gases, and also by synthesis (for example ethyl benzene and isopropylbenzene).

Divinyl is obtained by catalytic decomposition of ethyl alcohol and also by dehydration of butane and butylene in one or in two stages. Production of divinyl from alcohol by the method developed by S. Lebedev is an example of a catalytic, reversible, endothermic process. The process is described by the overall reaction equation



but it passes through a number of consecutive stages:



Simultaneously, side reactions occur. It follows that catalytic decomposition of ethyl alcohol is a complex chemical process; besides the main products up to 60 other different compounds (acetaldehyde, water, hydrocarbons, higher alcohols, etc.) are formed. The divinyl yield depends on the activity of the catalyst, the temperature of the catalytic reaction, the ratio of the basic components in the initial mixture, the presence of impurities, etc. In industry complex catalysts are employed which contain both dehydrating and dehydrogenizing components. Since the process occurs at a high temperature, heat must be added to raise the temperature of the gas mixture and to compensate for the endothermic effect. In this process  $k_{\text{overall}} = f(k_{\text{main}}, k_{1\text{side}}, k_{2\text{side}}, k_{3\text{side}}, \dots)$  and the increase in the rate of the side reactions with an increase in the temperature places a limit on the temperature, although according to the endothermic nature of the process it should be high. The use of improved catalysts with higher selectivity has resulted in increased yields of divinyl ( $x_a$ ) which at present have reached approximately 75 per cent of the theoretical value (with respect to alcohol decomposed). Since the

process is accompanied by an increase in the gas volume, decreasing the pressure favourably affects the divinyl yield.

The process involves the following basic operations: (1) evaporating the alcohol, (2) catalytic decomposition of the alcohol vapours, (3) recovery and purification of divinyl, and (4) regeneration or replacement of the catalyst. The alcohol is evaporated, the vapour is superheated, and at a temperature of 180-200 °C it enters into the superheater of the reactor furnace, where it is heated to 370-410 °C.

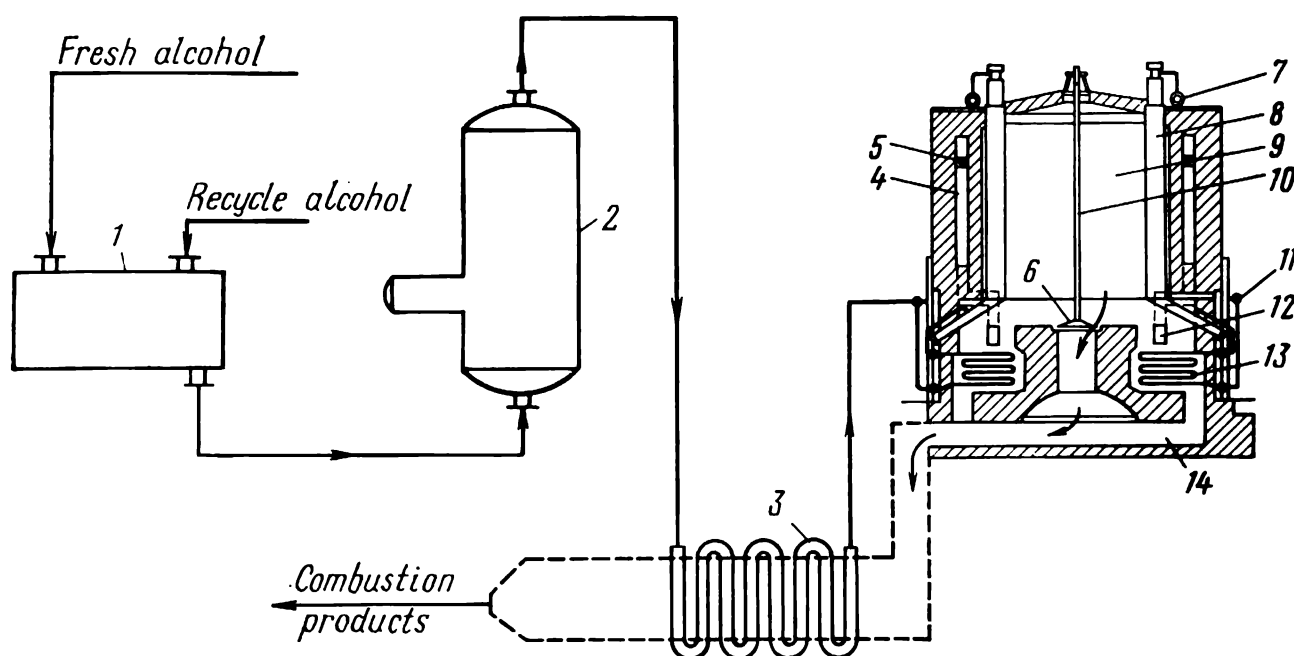


Fig. 81. Flow diagram of a unit for manufacturing divinyl (butadiene-1,3) from ethyl alcohol:

1—alcohol measuring tank; 2—alcohol evaporator; 3—central superheater; 4—furnace; 5—nozzle; 6—valve; 7—alcohol-vapour collector; 8—retort; 9—muffle; 10—rod; 11—converted-gas collector; 12—channel; 13—pipe-coil superheater; 14—flues

The catalytic reaction is carried out at 370-385 °C. The vapours then flow through the collector, the alcohol superheater below the retort and then enter the lower part of the retort.

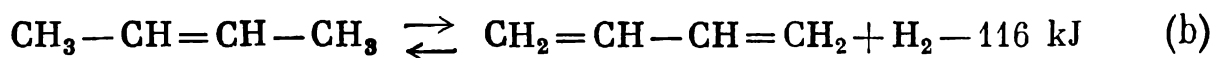
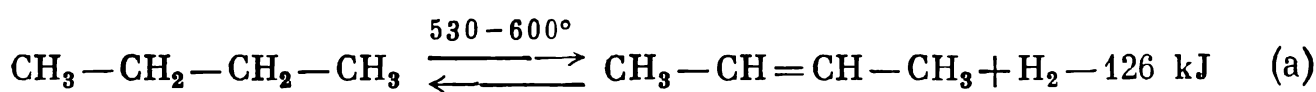
Catalytic decomposition of the alcohol, which takes place in catalytic-reactor furnaces (Fig. 81), is the most important of the operations. The furnace is lined with fire-brick and has double walls which form a narrow annular space, serving as the combustion chamber in which a liquid or gaseous fuel, fed through nozzles, is burned. The combustion products pass through channels into the alcohol superheater and then to the inner department of the furnace, which has retorts filled with the catalyst (16 or 24 of them) located around the perimeter. The catalyst is periodically unloaded through the branch pipe at the bottom of the retort. The gases from the furnace retorts enter a collector and at a temperature of 360 °C are directed to the unit for condensing and distilling the alcohol; on their way they pass through waste-heat boilers, where they are cooled to 180 °C.



The gases are subjected to condensation by cooling them with water and cold brine under a vacuum of 100-55 mmHg in a group of consecutive condensers. In them, most of the impurities and the unreacted alcohol residue condense, and the alcohol is then recycled to the process. The divinyl, which has a boiling point of  $-4.5^{\circ}\text{C}$ , is absorbed in ethyl alcohol; it is stripped from the alcohol solution and after careful purification enters the polymerization unit.

Catalytic dehydrogenation of butane and butylenes to butadiene is an important process of the synthetic-rubber industry. The separation of butadiene from the gases of petroleum stock pyrolysis is however the process with the best economic indexes. The use of selective catalysts makes it possible to carry out the process at a lower temperature, at which thermal cracking of the initial and intermediate compounds occurs to only a very small degree. Industrial catalysts promote disruption of the C—H bonds and simultaneously protect the C—C bonds.

Dehydrogenation of *n*-butane into divinyl initially forms *n*-butylenes after which divinyl is produced by further dehydrogenation:



The heat of the reaction depends on the structure of the initial compounds and therefore varies, however in rather narrow limits. The course of the dehydrogenation reactions depends on the composition and activity of the catalyst, the temperature, pressure, duration of the process and the presence of impurities in the starting materials. The yield of divinyl is limited not only by the thermodynamic equilibrium but also by hydrocarbon cracking reactions which proceed simultaneously.

Figure 82 shows how the equilibrium of the *n*-butane dehydrogenation reaction depends on the temperature and pressure. According to Le Chatelier's principle, lowering the pressure and raising the temperature should increase the yield of divinyl.

The dependence of the equilibrium constant of the reaction of dehydrogenation of *n*-butane to butylene on the temperature is expressed by the equation:

$$\log K_p = 7.574 - 30\,500/4.575T \quad (9.7)$$

and the dependence of the equilibrium-conversion degree on the pressure *P*—by the equation

$$x_p = \sqrt{K_p/(K_p + P)} \quad (9.8)$$

The optimal time of contact for converting *n*-butane to *n*-butylenes drops with a rise in the temperature, and at 550-575  $^{\circ}\text{C}$  over indus-

trial alumino-chromium catalysts it amounts to approximately 2 sec (Fig. 83). Conversion of *n*-butane in a single pass through the catalyst is 40-60 per cent, and the yield of *n*-butylenes is 35-40 per cent

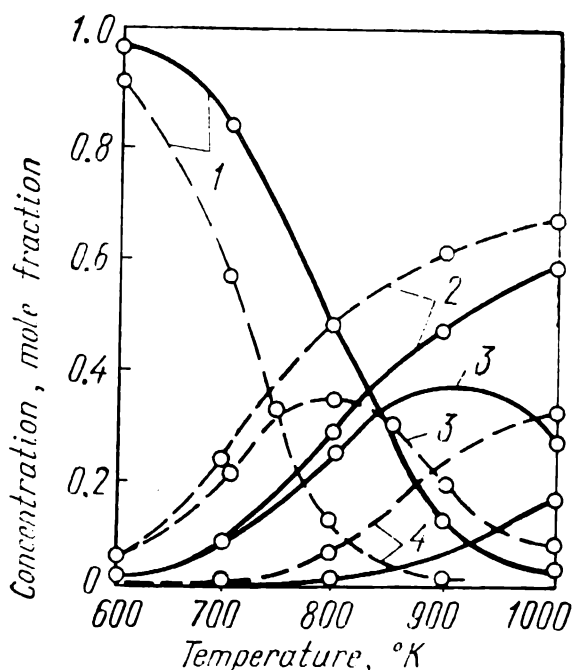


Fig. 82. Concentration of *n*-butane dehydrogenation reaction products at equilibrium:

1—*n*-butane; 2—hydrogen; 3—butylene;  
4—divinyl; — pressure = 1 atm;  
— — — — — pressure = 0.1 atm

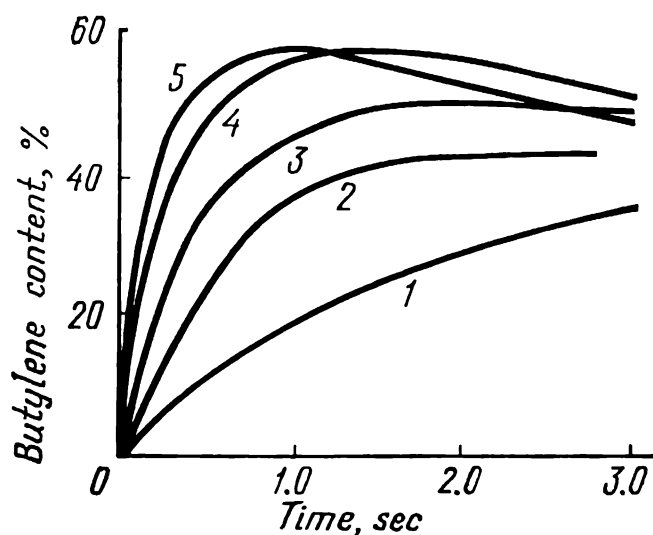


Fig. 83. Dependence of contacting time on the temperature of dehydrogenation of *n*-butane to *n*-butylenes:

1—525 °C; 2—550 °C; 3—570 °C; 4—600 °C;  
5—625 °C

with respect to the initial materials. The process of *n*-butane dehydrogenation is carried out either in one or two stages. A flow diagram showing the principle of the two-stage process for manufacturing divinyl from butane is given in Fig. 84.

Dehydrogenation of butane in a moving or a fluidized catalyst bed provides continuous action and raises the reactor capacity.

Dehydrogenation of *n*-butylenes is usually carried out in an adiabatic catalytic reactor (the catalysts are mixtures of metal oxides) at 600-650 °C together with superheated water vapour which is introduced to reduce the partial pressure of the reactant gases. The divinyl yield is 80-85 per cent with respect to the gaseous reaction products. The following equation has been proposed for calculating the reaction rate:

$$u = -\frac{dC_1}{d\tau} = k_1 \frac{C_1}{C_2^{0.5}} \left( 1 - \frac{C_2 C_3}{C_1 K_p} \right) \quad (9.9)$$

where  $C_1$ ,  $C_2$  and  $C_3$  are the concentrations of butane, butylenes and hydrogen, respectively;  $K_p$  the equilibrium constant.

From equation (9.9) it follows that the reaction products retard the butane-dehydrogenation process. The reaction of *n*-butylene

dehydrogenation is roughly of the first-order and the reaction products do not slow the process down.

$$u = -\frac{dC_2}{d\tau} = kC_2^{0.2} \quad (9.10)$$

When the period of contact is lengthened to above 0.2 second or the temperature raised above the optimal value the process selectiv-

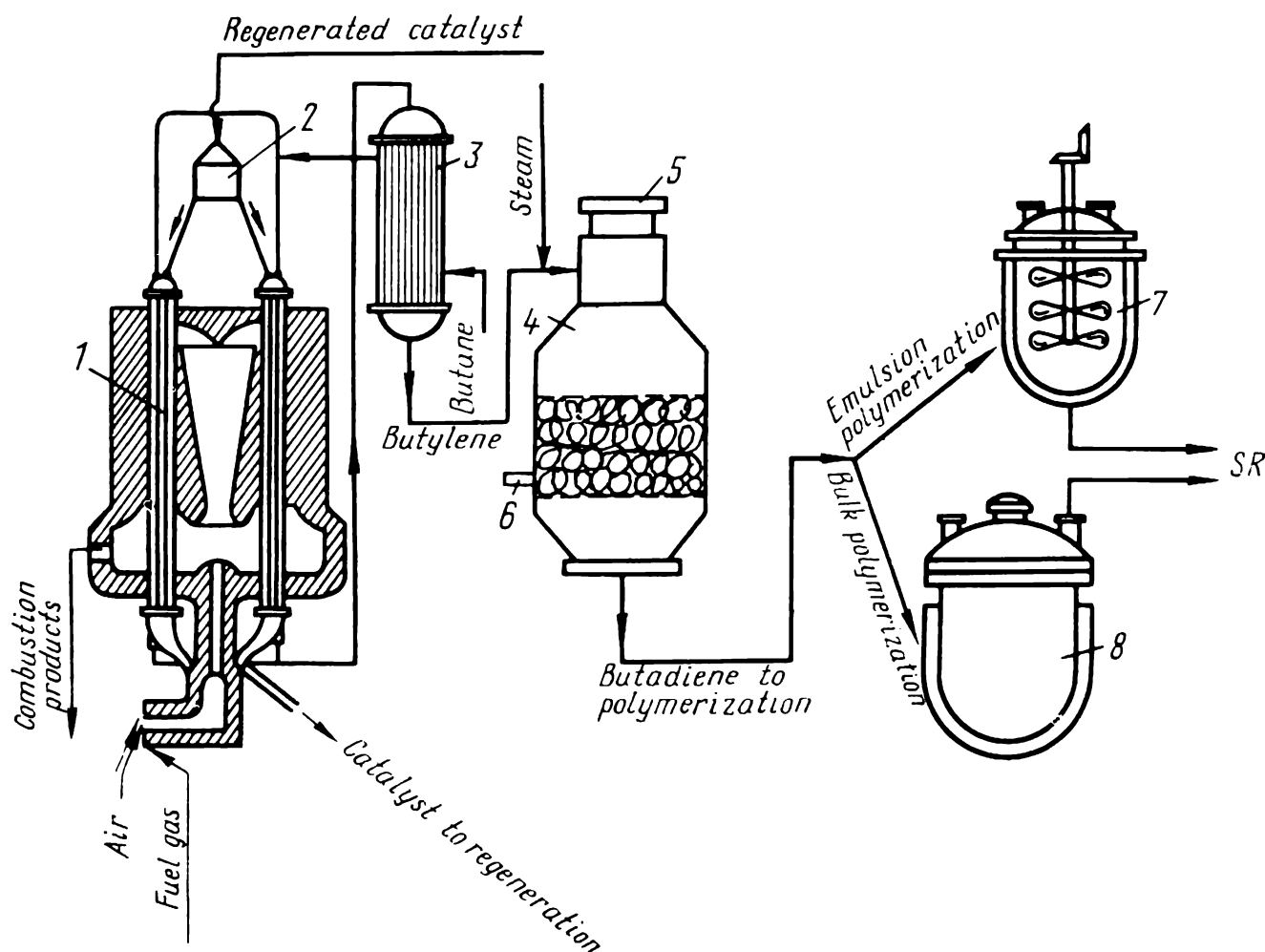


Fig. 84. Flow diagram for manufacture of divinyl and then rubber from butanes:

1—tubular externally heated reactor for dehydrogenation of *n*-butane to *n*-butylene; 2—regenerated catalyst silo; 3—heat exchanger; 4—adiabatic reactor; 5—catalyst-charging hatch; 6—catalyst-discharging hatch; 7—apparatus for emulsion polymerization; 8—apparatus for bulk polymerization

ity drops. The apparent activation energy of the reaction over mixed oxide catalysts (oxides of Fe, Cu, Mg, Cr, Zn and K) is 75-80 kJ/mole.

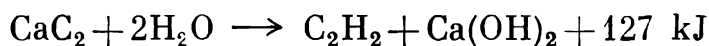
## 6. The Manufacture and Processing of Acetylene

Acetylene occupies a special place among the many gaseous hydrocarbons. The industrial uses of acetylene are exceedingly large numbered and diverse.

Since acetylene is an unsaturated chemical compound, its molecules easily enter into diverse chemical reactions, and the large number

of different acetylene derivatives obtained are used in manufacturing many very important substances. At present acetylene is produced both from calcium carbide and from hydrocarbon raw materials.

*Acetylene is manufactured by decomposition of calcium carbide in acetylene generators employing either a dry or a wet process, through the reaction:*



In the wet process, in generators operating by the "carbide into water" technique, crushed calcium carbide is fed at a uniform rate to a generator containing a large amount of water and the heat liberated in the process is transferred to the water. Water is taken in a tenfold excess with respect to the weight of the carbide consumed. The equipment necessary and especially the piping for removing the sludge formed and for recycling the water is very cumbersome. Besides, transportation, storage and utilization of a milk of lime suspension containing up to 70 per cent water present difficulties.

In the dry process, with generators operating by the "water into carbide" technique, water is added only in the amount necessary for the reactions and for removing the heat of reaction, by evaporating excess water. The process is carried out in the following manner. Calcium carbide is fed by a worm conveyer from a bunker through a seal to the top shelf of a generator ( $D = 3\text{--}5 \text{ m}$ ;  $H = 7.5 \text{ m}$ ; 11 shelves), of a design similar to that of a multihearth furnace for roasting pyrite (see Part I, Fig. 72c). The required amount of water is fed by a sprayer onto the upper shelf and the rakes move the thoroughly moistened calcium carbide in spiral paths from top to bottom, through holes located alternately at the centre and the periphery of the shelves (Fig. 85).

In its motion from shelf to shelf, the carbide is simultaneously agitated and it is converted practically in its entirety (98 per cent) to acetylene and  $\text{Ca(OH)}_2$ . The latter in the form of a dry powder (hydrated lime) is removed from the conical part of the generator with a stirrer by a worm conveyer. The acetylene liberated in the reaction, together with water vapour and entrained lime dust, at a temperature of about  $100^\circ\text{C}$ , flows to a scrubber, into which water is sprinkled. Here, the gas is cooled to  $20\text{--}30^\circ\text{C}$  and the dust is separated from it; the gas is then subjected to purification—hydrogen fluoride ( $300\text{--}600 \text{ mg/m}^3$ ), hydrogen sulphide ( $200\text{--}400 \text{ mg/m}^3$ ) and ammonia are removed.

The milk of lime formed is continuously withdrawn from the bottom of the scrubber to a thickener. Deposited sludge is pumped from the thickener to the drain system and the clarified water is returned to the scrubber, via a cooler, by a pump. The impurities are removed from the gas by scrubbing it with an aqueous solution of hypochlorite with active chlorine added or with a solution

of sodium bichromate in dilute sulphuric acid. The gas is dried and transported to the chemical processing section.

The carbide process is relatively simple but it has a number of significant drawbacks, primarily, the large size of the equipment, high electric-power consumption for making the carbide (10-11 kWh per kg acetylene) and the difficulty of utilizing waste products, which are

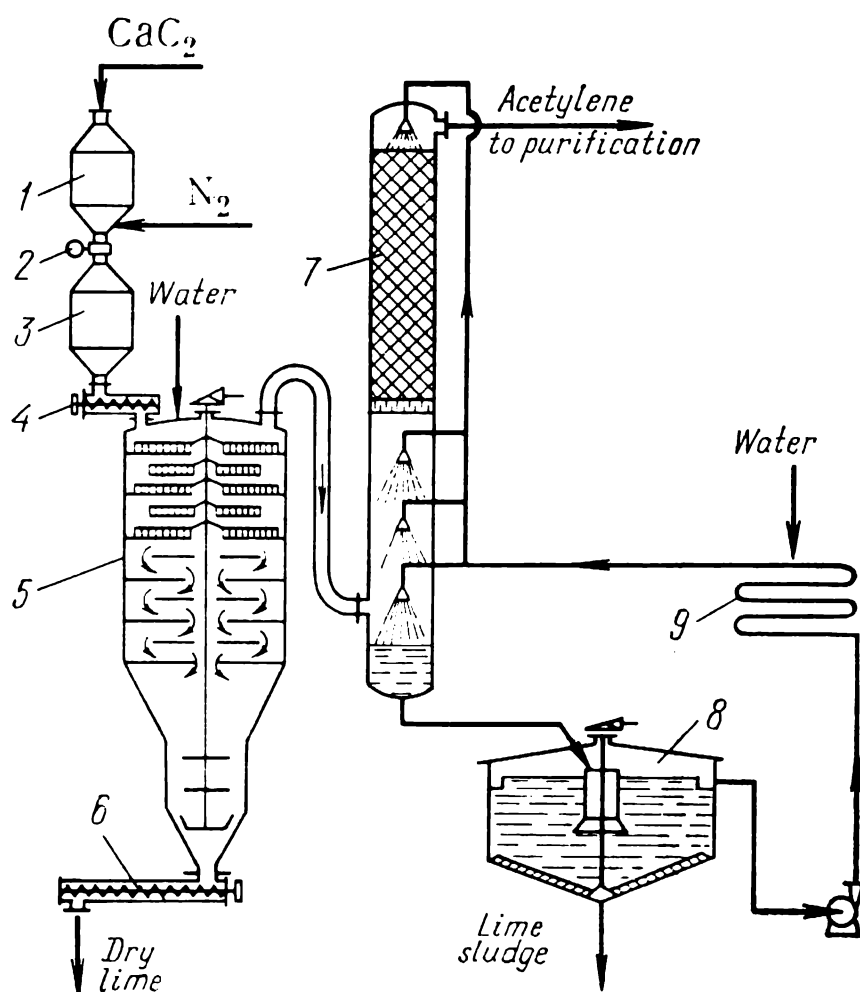
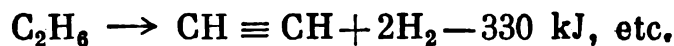


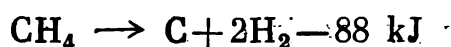
Fig. 85. Flow diagram of process for acetylene manufacture from calcium carbide:

1—hopper; 2—automatic seal; 3—buffer hopper; 4—worm-conveyer feed; 5—acetylene generator; 6—worm conveyor for lime removal; 7—scrubber; 8—thickener; 9—cooler

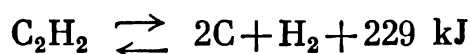
produced in large amounts. In recent years more efficient industrial processes have been developed, in which acetylene is made from hydrocarbon raw materials. The process, in which acetylene is produced from methane and its homologues (for example, ethane) by heating them in the absence of air, can be described by the following cracking reactions:



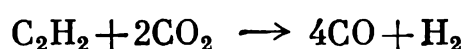
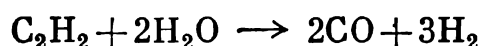
A side reaction is:



By raising the temperature and lowering the pressure, the process equilibrium can be shifted towards formation of the end product. However, at temperatures of 1400-1500 °C acetylene and the hydrocarbons are thermodynamically unstable; they decompose to form carbon black and hydrogen



or the acetylene reacts with other gases or water vapour present:



At 1400-1500 °C conversion of methane to acetylene takes place at a higher rate than decomposition of acetylene to the elements. This fact and the use of quenching make it possible to obtain acetylene. The equilibrium yield of acetylene from methane in the reaction at atmospheric pressure increases with the temperature:

Temperature, °K	C <sub>2</sub> H <sub>2</sub> , per cent
500	0.00
1000	1.53
1200	11.8
1400	46.2
1800	96.54
2200	99.68

However, at lower temperatures the rates of the principal reactions are very low. Therefore, to achieve maximum acetylene yield and reduce various side reactions, high volumetric rates of gas flow are used, so that the raw materials are at temperatures above 1400 °C only during a period of thousandths of a second. The products formed are quickly cooled ("tempered") to prevent decomposition of the acetylene.

*The following processes are in use for making acetylene from natural gas and other hydrocarbon gases:* (1) electrical cracking of gaseous hydrocarbons or of liquid hydrocarbon products (tars and heavy petroleum residues); (2) thermal cracking; and (3) thermal-oxidizing pyrolysis.

*Electrical cracking* is carried out in a reactor (Fig. 86), in which an electric arc is created by a direct electric current between electrodes. The initial gas mixture, under a gauge pressure of 0.5 atm, tangentially and at a high velocity (over 100 m/sec), enters the top, wider part of the reactor having the form of a hollow steel cylinder. Then the gas passes through the arc zone (1600 °C) and leaves the reactor via a narrow tube, cooled with water, which serves as the anode. The gases, which have an extremely high rate of flow at this point (600-1000 m/sec), are at a temperature of 600 °C at the outlet from the tube; they are flash-cooled to 150 °C by direct injection of water

("tempering"). The superheated steam formed by evaporation of the water leaves the apparatus together with the gas reaction mixture. For separating acetylene from it, various solvents are used: water, acetone, dimethylformamide and others. A starting-up electrode is used for "igniting" the arc to put the reactor into operation. Consumption of electric power per 1 kg concentrated acetylene produced is approximately 10 kWh. Methane conversion in a single pass through the reactor amounts to 40-50 per cent. The acetylene content of the gas amounts to 14%.

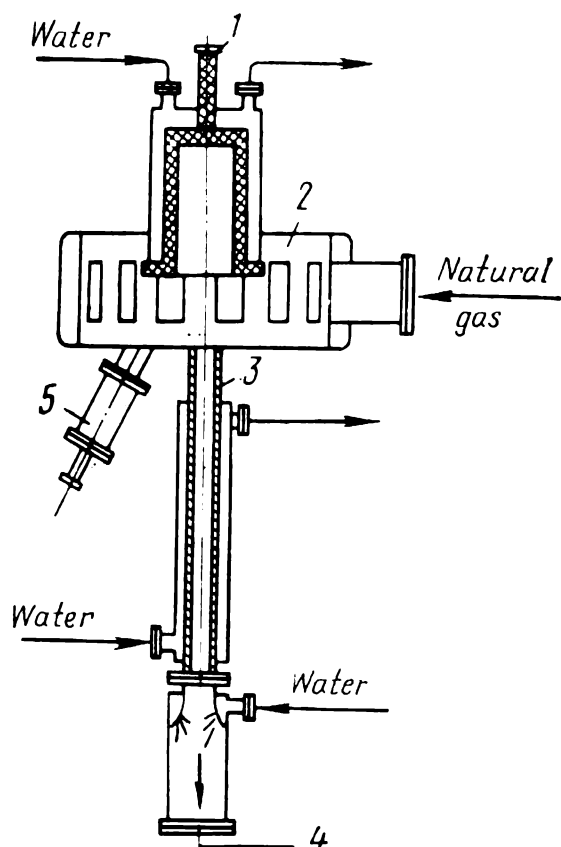


Fig. 86. Reactor for electrical cracking:

1—cathode; 2—reaction chamber; 3—grounded anode; 4—cracking-gases exit; 5—starting-up electrode

This method can be used for processing both methane of natural gas and vapours of methane homologues, and this is one of its positive features.

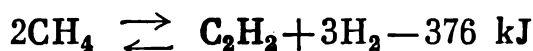
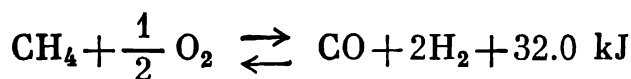
*Thermal cracking* is carried out in regenerator-furnaces at 1450-1600 °C. The gas is brought into contact with the surface of a preheated packing. If two furnaces connected to one combustion chamber are used the process can be carried out continuously by the following cycle, one minute of heating the packing and one minute of cracking which provides maximum utilization of the heat

of the reaction. Propane is processed in the Soviet Union by cracking it in pipe stills at a temperature of 1100-1200 °C, contacting time of 0.1-0.15 sec and residual pressure of 380 mmHg.

*Thermal oxidizing cracking* (pyrolysis) is a more extensively used process. The heat required for the reactions is produced by combustion of part of the methane.



The basic pyrolysis reactions are:



A temperature of approximately 1450 °C is maintained in the pyrolysis furnace. Oxygen is taken in a volume ratio of 60-65 per cent with respect to the methane. Both gases are separately preheated to

400-600 °C and fed at a high rate to the reaction channel, the residence time in it being 0.003-0.006 second. Furnaces developed in the USSR are very compact, they have high operating capacities at low oxygen consumption. Both single-channel and double-channel reactors are used. Conversion of the methane into acetylene amounts to 30 per cent.

It has been found that the introduction of gasoline into the tempering zone can significantly increase the yield of acetylene, ethylene and synthesis gas. Since the composition of the end-product gas considerably depends on the pyrolysis process employed and the composition of the raw material, the schemas used for separating the acetylene from the other gases may differ widely from unit to unit.

In making acetylene from methane large amounts of hydrogen and other gases are formed together with the principal product (Table 15). Thus, the amount of hydrogen produced per ton of acetylene is sufficient to make 3-4 t ammonia from it. Electrocracking also produces 50-100 kg carbon black. The gases of thermal oxidizing cracking contain carbon monoxide and hydrogen in the ratio necessary for synthesizing hydrocarbons or methanol (1 t of methane yields approximately 1160 kg of synthesis gas).

TABLE 15

Representative Composition of Gases Obtained  
by Processing Natural Gas

Process	Gas composition, % by volume						
	C <sub>2</sub> H <sub>2</sub>	C <sub>2</sub> H <sub>4</sub>	CH <sub>4</sub>	H <sub>2</sub>	CO	CO <sub>2</sub>	Other products
Electrical cracking	13.3	0.9	27.5	48.4	—	—	9.9
Thermal cracking	10.0	3.8	15.0	55.7	6.9	1.6	7.0
Thermal oxidizing cracking (pyrolysis)	8.5	0.6	6.0	54.0	26.0	3.7	1.2

One of the most important industrial processes is that of the *manufacture of acetaldehyde*. It can be made from acetylene by three methods: (1) by hydration of acetylene in the liquid phase employing a mercury-iron catalyst (the Kucherov method discovered in 1881); (2) by hydration of acetylene in the vapour phase over a solid catalyst; (3) by hydrolysis of simple vinyl ethers. Acetaldehyde is also made by partial catalytic oxidation of ethyl alcohol and by catalytic oxidation of ethylene (the most promising method).

Production of acetaldehyde by the Kucherov reaction is carried out in industry according to the flow diagram given in Fig. 87. Care



fully purified acetylene together with recycle gas at a pressure of 1.5-2.5 atm is continuously bubbled in a hydrator (15 m high, 1.34 m in diameter at the narrow part) through a liquid catalyst containing a solution of mercury (II) sulphate in sulphuric acid. Since acetal-

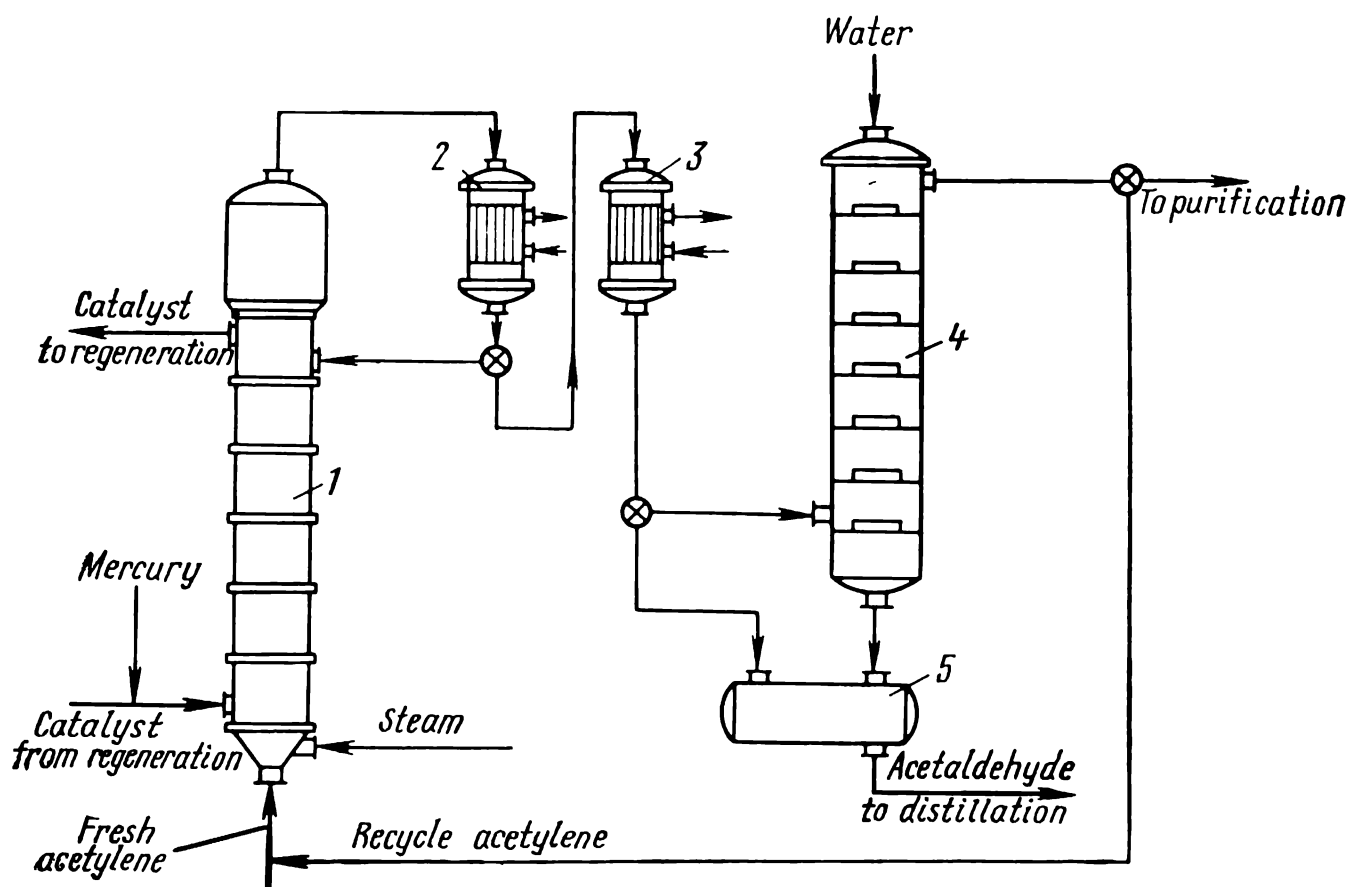
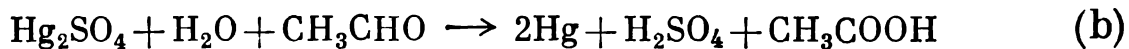


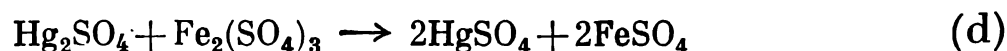
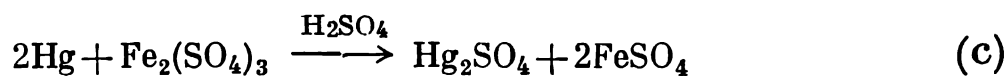
Fig. 87. Flow diagram of the manufacture of acetaldehyde by liquid-phase hydration of acetylene:

1—bubbler-type hydrator; 2 and 3—shell-and-tube coolers; 4—tray tower; 5—acetaldehyde tank

dehyde is a strong reducing agent, in the process mercury (II) is reduced to mercury (I) and then to the metal:

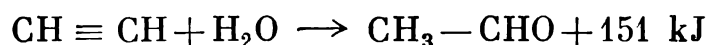


To maintain the necessary composition of the catalyst liquid, metal mercury and an oxidizing agent are added which in the presence of sulphuric acid transform the mercury into the mercury (II) sulphate required for the hydration process:



The mercury metal is introduced periodically; it is sprayed into the reactor through a funnel at the top (approximately 0.1 kg of

mercury is lost per ton of acetaldehyde produced). Under these conditions 50 to 60 per cent of the acetylene is hydrated by the reaction:



The apparatus—a tower which is wider at the top so as to separate entrained liquid spray and to contain foam formed—is made of ferrosilicon or of stainless steel. Each of the bubbler trays of the hydrating tower operates in accordance with a model which is closer to complete mixing than to plug flow both with respect to the gas and the liquid. The gas and liquid move through the tray in cross flow. However, since there are a large number of trays in the tower process calculations can be carried out for counter-current plug flow through the tower.

The temperature in the hydrator is maintained between 90 and 100 °C by introducing live steam. The gases leaving at the top of the hydrator, which contain acetaldehyde, unreacted acetylene, water vapours and other impurities, are passed through coolers. In the first the water vapour condenses, the condensate being returned to the hydrator, and in the second acetaldehyde and water condense together and the solution collects in a tank. The gases which do not condense are fed into an absorber, where the remaining aldehyde is removed with water cooled to 10 °C and the unreacted acetylene from the tower is recycled to the head of the process. Approximately 10 per cent of the gas is continuously purged to remove nitrogen and carbon dioxide, and prevent their excessive accumulation in the recycle gas. The acetaldehyde solution formed is distilled.

The catalyst liquid flows out of the hydrator to a settling tank (for recovering mercury) and from it goes to a regeneration unit. The catalyst liquid contains approximately 200 g/l sulphuric acid, 0.5-0.6 g/l mercuric oxide and 40 g/l iron oxides.

The acetaldehyde yield with respect to the acetylene reacted amounts to 90-95 per cent. To produce 1 t of acetaldehyde 680 kg of acetylene, 0.1 kg of mercury, approximately 3 t of steam and also a certain amount of sulphuric and nitric acids and iron sulphate are consumed. The process yields as co-products acetic acid, crotonic aldehyde and paraldehyde.

Since mercury is extremely toxic and its use is undesirable from the point of view of health safety, it has been suggested that other, non-mercury, catalysts, e.g. oxides of Zn, Mg, Ni, Fe, Co, Cr and other metals and also some salts and acids, be used. Heterogeneous catalytic processes of this type can be carried out using a fluidized bed of the catalyst. The yield of acetaldehyde amounts to 88-90% of the converted acetylene. The degree of acetylene conversion in one pass through the reactor is approximately 50%.

*Acetic acid* has been manufactured for a very long time by dry distillation of wood and fermentation of ethyl alcohol, and since the

beginning of the 20th century it is also being made synthetically by oxidation of acetaldehyde or hydration of ketene. In the acetaldehyde oxidation process, oxygen of the air in the presence of manganese salts first yields peracetic acid:



It reacts with a second molecule of acetaldehyde to produce two molecules of acetic acid:



Accumulation of peracetic acid in the process apparatus may result in an explosion. To prevent this, the gas-vapour mixture is diluted

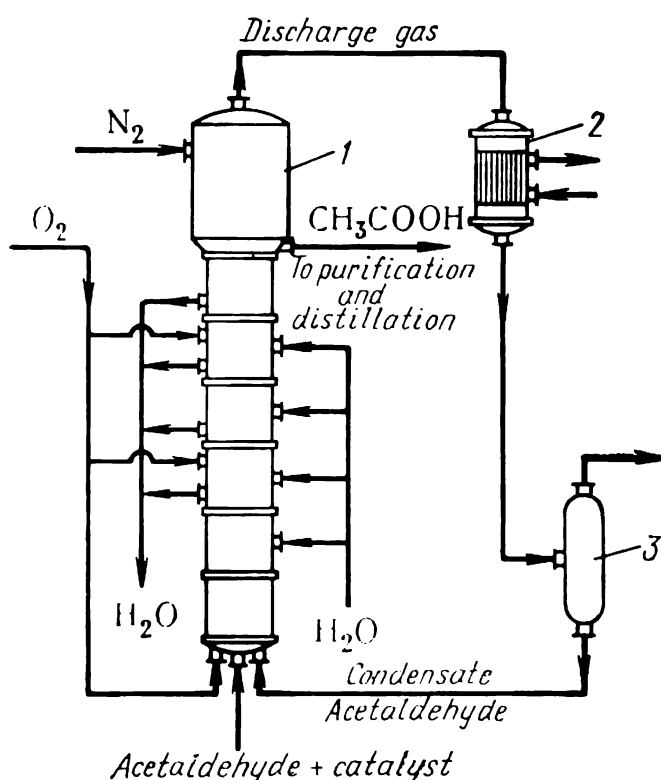


Fig. 88. Flow diagram of the manufacture of acetic acid by oxidation of acetaldehyde:

1—oxidation tower; 2—condenser; 3—separator

with nitrogen and the temperature is kept between 60 and 75 °C. The use of manganese salts as a catalyst promotes the reduction of peracetic acid to acetic acid. The process is carried out in a tray-type oxidizing tower, similar to that used in making acetaldehyde. The industrial process consists of three stages: (1) oxidation of the acetaldehyde; (2) absorption of the acetaldehyde from the discharged gases; and (3) separation of acetaldehyde from acetic acid.

A solution of acetaldehyde and the catalyst—a solution of manganese acetate—are introduced at the lower part of the tower (Fig. 88). The reaction mixture fills the entire tower with the exception of the upper part, into which nitrogen is fed to prevent the vapours from

exploding. In several spots at various heights oxygen is introduced into the tower. Oxidation is carried out at 60-70 °C and a pressure of 2 atm. The heat liberated is removed with the circulating liquid and by means of a water jacket or water-cooler coils.

The acetic acid formed together with the reaction co-products (acetic anhydride, formic acid, water, etc.) is withdrawn and subjected to purification and distillation. The mixture of the vapours of acetaldehyde, acetic acid and other substances discharged from the top of the tower is directed to a cooler-condenser and then to a separator, from which unreacted acetaldehyde is returned to the reactor tower. The exhaust gases are scrubbed and released to the atmosphere.

### **1. The Economic Importance of High-Molecular Compounds**

Natural and synthetic high-molecular organic compounds, such as cellulose, chemical fibres, plastics, rubber, vulcanized rubber goods, varnishes, adhesives, artificial leather and fur, films, etc. are of tremendous economic importance. Both natural and synthetic high-molecular compounds possess a multitude of remarkable properties. They may be elastic or rigid, hard or soft, transparent or opaque and may combine most surprising properties: the strength of steel and low density, elasticity with heat- and sound-insulating properties, chemical stability and hardness, etc. Due to such a universality of different properties and the ease with which they can be mechanically processed, high-molecular compounds can be employed for manufacturing parts and structures of any shape, size, or colour. Progress in the fields of aviation, machine- and shipbuilding, electronics and electrical engineering, jet propulsion and nuclear engineering would be impossible without the use of synthetic materials.

Plastics can be employed for making the hulls of ships, bodies of automobiles and tractors, parts of machines, insulation, etc. The use of plastics in machine-building has made it possible to find new solutions for complicated design problems, achieve higher productivity, lower the cost of the machines and improve their operating properties.

High-molecular-compound coatings on metals, wood and concrete afford reliable protection from corrosion. Individual parts and entire units can be coated with sheets of plastic, rubber, or covered with films, varnishes or enamels. The new synthetic materials supplement agricultural origin raw materials, and their use has made it possible to increase production of cloth, clothes, shoes, furs, and various other consumer goods.

### **2. Properties, Classification and Methods of Manufacturing High-Molecular Compounds**

High-molecular compounds can be divided into artificial compounds, made by recovering, purifying and reforming natural polymers (cellulose, proteins, lignin, nucleic acids, natural rubber, wool, silk, etc.), and synthetic compounds, which are manufactured from various low-molecular organic compounds.

High-molecular compounds consist of giant molecules (macromolecules), formed by chemical reactions between a large number of the initial monomer molecules. Whereas the molecular weight of low-molecular substances (water, alcohols, acids, salts, etc.) amounts to tens of units, the molecules of high-molecular compounds (polymers) can contain hundreds or thousands of atoms joined together by main-valency bonds, and they have molecular weights which often amount to thousands, or even millions, of units.

High-molecular compounds differ from monomers both in their properties and appearance. The macromolecules consist of a large number of repeating elementary links (see Table 16). The number of these links in the high-molecular compound chain is called the degree of polymerization (*n*).

TABLE 16

Initial Compounds and Basic Links of Some High-Molecular Compounds

Polymer	Initial monomer	Basic link
Polyethylene	$\text{CH}_2=\text{CH}_2$	$-\text{CH}_2-\text{CH}_2-$
Polyvinyl chloride	$\text{CH}_2=\text{CH}$   Cl	$-\text{CH}_2-\text{CH}-$   Cl
Polystyrene	$\text{CH}_2=\text{CH}$   $\text{C}_6\text{H}_5$	$-\text{CH}_2-\text{CH}-$   $\text{C}_6\text{H}_5$
Polytetrafluoroethylene (Fluoroplastic-4)	$\text{CF}_2=\text{CF}_2$	$-\text{CF}_2-\text{CF}_2-$
Polyacrylonitrile	$\text{CH}_2=\text{CH}$   CN	$-\text{CH}_2-\text{CH}-$   CN
Polyisobutylene	$\text{CH}_2=\text{C}-\text{CH}_3$   $\text{CH}_3$	$-\text{CH}_2-\text{C}-\text{CH}_3$   $\text{CH}_3$
Polybutadiene	$\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	$-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$ or $-\text{CH}_2-\text{CH}-$   $\text{CH}=\text{CH}_2$
Natural rubber	$\text{CH}_2=\text{C}-\text{CH}=\text{CH}_2$   $\text{CH}_3$	$-\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2-$   $\text{CH}_3$
Polycaprolactam (capron)	$\text{OC}(\text{CH}_2)_5\text{NH}$ └──────────┘	$-\text{C}-(\text{CH}_2)_5-\text{N}-$                        O                   H

The degree of polymerization  $n$  increases in the course of the reaction and may become very large. However,  $n$  is a mean value, i.e. at any moment during polymerization or polycondensation the reaction product is a mixture of particles with various molecular weights

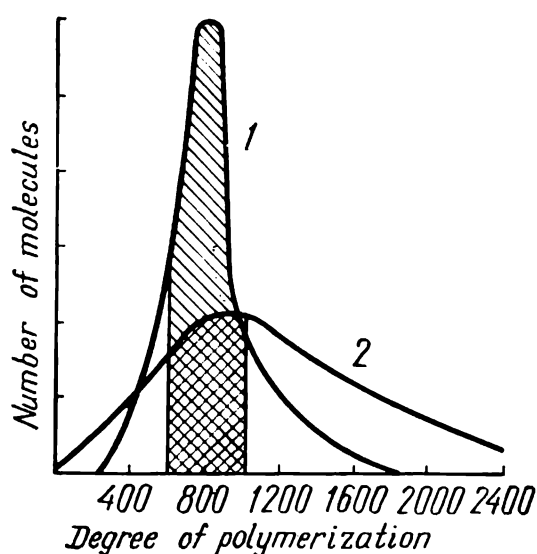


Fig. 89. The distribution of molecules with different length:

1—nitrocellulose; 2—polystyrene

(Fig. 89). Nitrocellulose (curve 1) and polystyrene (curve 2) both have a mean degree of polymerization of approximately 800, however the number of molecules with this degree of polymerization is three times larger for cellulose than for polystyrene (the cross-hatched region). These distribution curves show that the maximum degree of polymerization of nitrocellulose is 1700, whereas polystyrene has many molecules with a degree of polymerization above 2400.

It follows, that high-molecular compounds are a complex mixture of molecules with different degrees of polymerization. A polymer, therefore, can only be described by the mean value of the molecular weight. Consequently, the molecular weight of a polymer ( $M$ ) is equal to the product of the molecular weight of an elementary link ( $m$ ) and the degree of polymerization ( $n$ ):

$$M = mn \quad (10.1)$$

There are certain properties which are common to all high-molecular compounds. The compounds are, as a rule, highly insoluble, with the solubility usually decreasing as the molecular weight increases. Ordinarily, dissolution occurs very slowly and it is often preceded by swelling, as the molecules of the solvents penetrate into the body of the polymer being dissolved. The solutions obtained are extremely viscous even at low concentrations. There are high-molecular compounds which are absolutely insoluble.

Polymers are not volatile and do not have a distinct melting point; when heated they gradually soften and melt but many of them decompose without melting. The larger the size of a polymer molecule, the higher is the temperature at which it softens and melts.

The tremendous molecular weight and the corresponding intermolecular forces give the polymers high strength (Fig. 90) and also give elastomers the capacity of large reversible deformations. High-molecular compounds with very diverse properties can be obtained by changing the structure and length of the chain, the order of the links

making up the polymer molecule, the composition of the initial monomers, the conditions in which the synthesis is carried out and the conditions of subsequent processing. Polymers contain crystalline zones and also regions where the macromolecules are not arranged in any fixed order, i.e. amorphous regions. With growth of the cry-

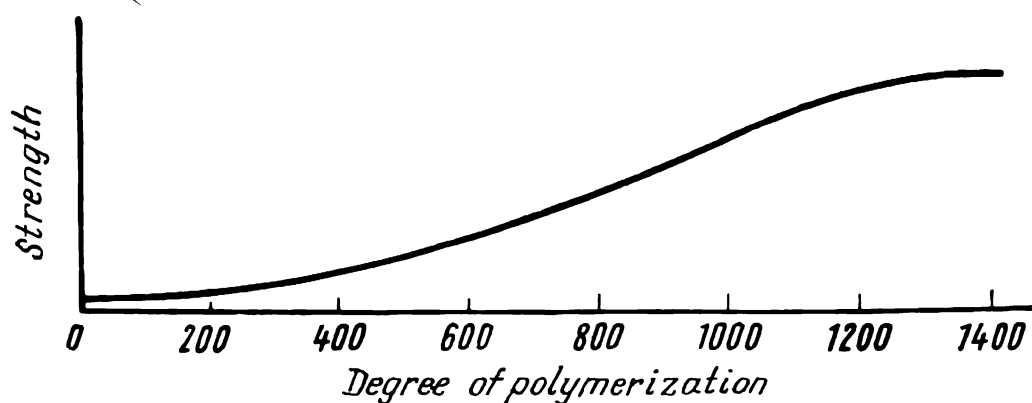


Fig. 90. The change in strength of cotton fibres with molecular weight

stalline regions of high-molecular compounds, their strength and hardness increase. A feature of highly-crystalline chemical fibres is high strength; whereas rubber has an amorphous structure. When a rubber is heated it changes from a vitreous state to a highly elastic

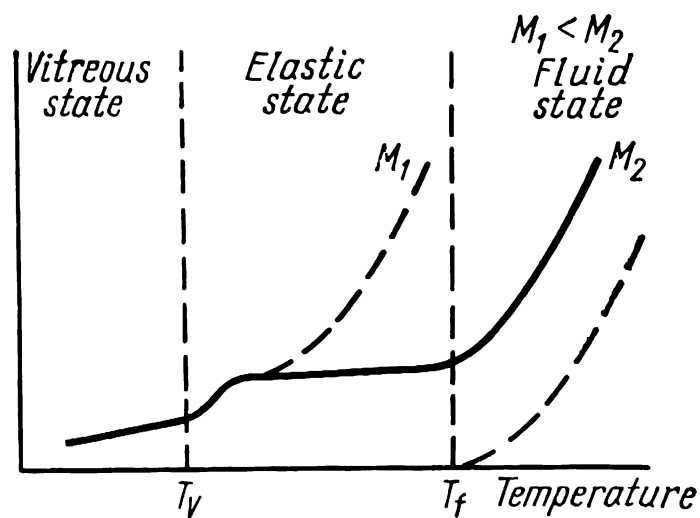


Fig. 91. The change in the deformation of polymer with temperature at a fixed load

one. The dependence of the deformation under a fixed load on temperature is shown in Fig. 91 for polyisobutylene. As can be seen from this figure, three regions with different states of the high-molecular compounds can be distinguished: a vitreous one, a region of high elasticity and a region of fluid flow. The location of the borders between the regions depends on the size of the macromolecules and the structure of the polymer.



The degree of polymerization, or the molecular weight, to a large extent determines not only the properties of the polymer produced, but its applications as well.

**High-molecular compounds are classified** according to various properties, for instance, according to their origin (as natural or synthetic), according to the chemical composition of the basic chain, the structure of the macromolecules, physical properties, the manufacturing method, the method utilized for remaking them into finished ware, etc. High-molecular compounds made up of links of one and the same monomer are known as homopolymers, and those in which the links are different monomers are called heteropolymers or copolymers.

Polymers can be divided into three groups according to the chemical composition of the basic chain.

In **carbon-chain** polymers the basic chain consists entirely of carbon atoms, as, for example, in polyethylene, polyisobutylene, polyvinylchloride, polybutadiene, etc. (see Table 16).

**Hetero-chain** polymers along with the carbon atoms contain also atoms of oxygen, nitrogen, silicon, phosphorus or other elements in the basic chain. Cellulose, proteins, polyamides (for instance, capron), polyesters, polyurethane, siliconorganic polymers are examples.

**Hetero-organic** polymers have a basic chain containing atoms of silicon, aluminium, titanium, phosphorus or other elements, which are not a part of natural organic compounds, and side chains made up of carbon groups. Distinguishing features of such polymers are, as a rule, high strength, hardness and resistance to high temperatures.

**Linear, branched and three-dimensional** structures of the macromolecules are distinguished, depending on the positions occupied by the elementary links. Each of these groups has its subdivisions. Thus, linear macromolecules may have a straight, zigzag (polyethylene) or cyclic-chain (polyphenylene).

In a *linear structure* each elementary link is joined to only two neighbouring ones and the molecule has the form of a filament. In this case there is uniform "load-distribution" throughout the entire chain:  $-l-l-l-l-l-l\dots$ , where  $l$  represents an elementary link.

Such filament-form molecules may be arranged in parallel—for instance, in fibres—or they may be intertwined or rolled into balls, as in rubber. This structure is found in polyethylene, polypropylene, cellulose, polyesters, polyamides and many other high-molecular compounds used in manufacturing fibres, films, plastics, rubber, etc. Polymers with molecules of this form possess high strength and elasticity; they can be dissolved and, as a rule, fused.

During the course of molecular synthesis, long chains may branch out to form a structure with side branches, which are shorter than the

basic chain (Fig. 92). Molecules of starch, some resins in an intermediate stage of resin formation, and so-called graft polymers are of this type. Branched polymers dissolve and fuse less readily than linear ones do.

Linear and branched molecules under certain conditions may be linked to neighbouring ones by bridges consisting of atoms or groups

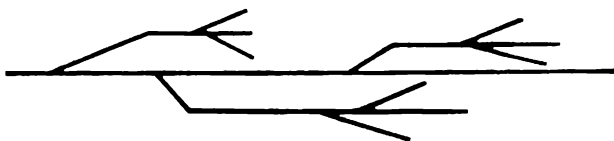
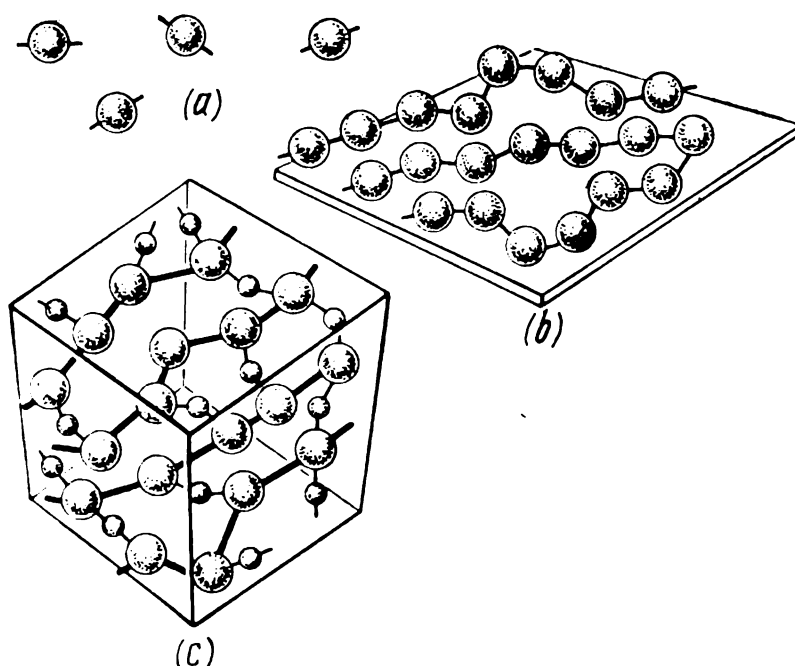


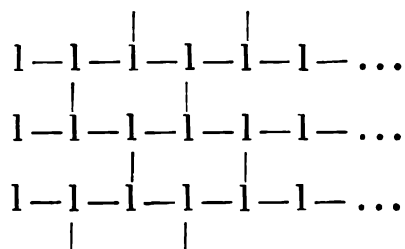
Fig. 92. Branched-structure high polymer



**Fig. 93. Links between monomers in a polymer molecule:**

(a)—monomers; (b)—polymer with linear links; (c)—polymer with three-dimensional links

of atoms, to form “cross-linked” molecules. An increase in the number of bridges results in a three-dimensional structure of unlimited size (Fig. 93):



Compounds with a structure of this type depending on the number of bridges can be either hard or rubberlike, they do not melt, are insoluble, but some of them do swell to a limited extent. Examples are rubber, phenol-formaldehyde- and urea-formaldehyde resins in

the final stage of resin formation. With growth of the number of cross ties the fluidity of the polymer is reduced and finally it loses its high-elasticity and plastic properties.

According to their physical properties all polymers can be divided into two large classes: **plastomers**, the salient features of which are high strength, high Young's modulus values and poor elasticity, and **elastomers**—natural and synthetic rubbers, gutta-percha, polyisobutylene and other compounds, which have low Young's modulus values and high elasticity. These rubber-type polymers can be stretched to a size tens of times larger than the original one.

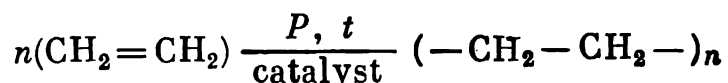
High-molecular compounds are divided, depending on their behaviour when heated, into thermoplastic and thermosetting polymers.

**Thermoplastic polymers** (or copolymers with a linear structure) soften when heated and harden again upon cooling recovering all their original properties: solubility, capability of melting, etc.

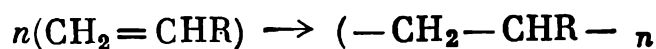
**Thermosetting polymers** when heated at first become plastic, but then, in the presence of catalyst or curing agent, a three-dimensional structure is formed; they solidify and lose their capability to fuse and to dissolve.

*According to the method by which the compounds are obtained* they are divided into polymerization- and polycondensation high-molecular compounds. In both cases the molecules of the initial substance used for their synthesis must contain either multiple carbon-carbon bonds, unstable cyclic groups, or functional groups ( $=C=C=$ ,  $-C\equiv C-$ ,  $=C=N-$ ,  $=C=O$ ,  $CH_2=CHX$ , where X is a halogen-, oxide-, amino-, cyan-, etc. group) capable of reacting with each other or with other molecules to form polymers.

**Polymerization** is the name of a process in which a number of molecules of a monomer unite to form a large, polymer molecule with an elemental composition identical to that of the initial monomer:

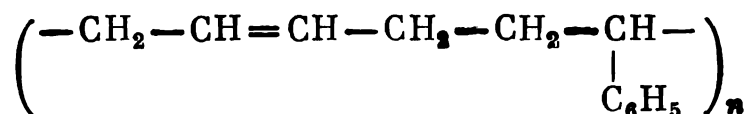


or in the general form:

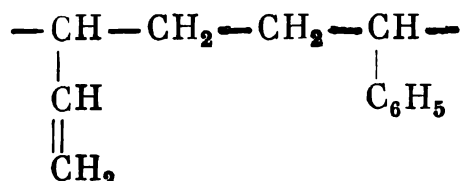


where R is a substituent. In the process no side products are formed. Increasing the reaction time results in an increased yield of the polymer and in an increase of its mean molecular weight. When unsaturated compounds polymerize the double bonds in the molecules "open" and as a result of the formation of free valencies a large number of the monomer molecules join together. When cyclic compounds polymerize the free valencies are formed by opening the ring. Joint polymerization (copolymerization) of two or more monomers is also a widely used reaction, which can be employed to obtain materials

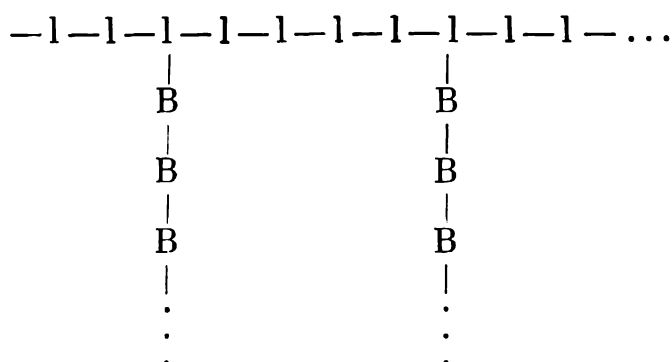
with diverse new properties, among them insoluble and non-melting substances. Copolymerization of butadiene and styrene forms butadiene-styrene rubber, which differs in its properties from ordinary, butadiene, synthetic rubber. This copolymer has the following elementary link:



or



In recent years new synthesis methods, such as graft polymerization and bulk polymerization, have been developed. In the first of these another monomer compound is grafted onto the basic chain of the polymer and is then polymerized. The side branches consist of links of compound B



Compounds with new properties were produced in this way. As an example, side chains of polystyrene were grafted onto polyethylene films.

Bulk polymerization is carried out by cleaving molecules of two different polymers into short chains (for example, during rolling or extrusion), following which the pieces, or blocks, produced are "joined" to form a polymer, in which blocks of the first compound (A) and the second (B) alternate. Thus, interaction of rubber and epoxide resins produces a polymer of exceptionally high resistance to attrition. In the same way rubber and polystyrene unite to form an impact-proof polystyrene, which does not crack when nails are driven into it.

Bulk polymerization can also be carried out by reactions between end functional groups of polymers or by joining macromolecules of various polymers to each other



Two types of polymerization reactions are employed in industry: stepwise polymerization and chain polymerization: (1) in *stepwise*

polymerization combination of molecules is accompanied by a transfer of hydrogen atoms and formation of intermediate compounds with a considerable lifetime, (2) in *chain* polymerization a molecule is first activated and this initiates polymerization of a large number of other molecules when it collides with them. In this case the intermediate products are not stable.

The principal products of stepwise polymerization are polymers with a low molecular weight. In contrast to stepwise polymerization chain polymerization does not stop at some intermediate stage and the end product is a high-molecular compound.

**Chain polymerization**, one of the most important methods used for synthesizing resins, consists of the stages: process initiation, chain growth and chain termination (see Part I, Chapter 4). The overall reaction can be represented as follows:

		<i>Rate constant</i>	<i>Rate</i>
Chain initiation	$M \rightarrow M_1^\bullet$	$k_i$	$u_i$
Chain growth	$M_1^\bullet + M \rightarrow MM_1^\bullet$	$k_g$	$u_g$
	$\vdots \quad \vdots \quad \vdots \quad \vdots \quad \vdots$		
	$M_{n-1}^\bullet + M \rightarrow M_n^\bullet$	$k_g$	$u_g$
Chain termination	$M_n^\bullet + M_m^\bullet \rightarrow M_{n+m}$	$k_t$	$u_t$

Chain polymerization can be started (initiated) (1) photochemically: by irradiation with artificial light, sunlight, etc.; (2) by radiation, for example, with  $\gamma$ -rays or by a high-frequency electric current; (3) thermally (by heating); (4) catalytically; (5) by initiators, i.e. compounds which accelerate polymerization but, in contrast to catalysts, are irreversibly consumed in the process.

If we assume that the chain-growth rate-constant,  $k_g$ , is the same for all the stages and, consequently, does not depend on the size of the radical, the overall rate of monomer conversion will be

$$-\frac{d[M]}{d\tau} = u_i + u_g = u_i + k_g[M][M^\bullet] \quad (10.2)$$

where  $[M^\bullet]$  is the concentration of all the polymer radicals;  $[M]$  the concentration of the monomer molecules;  $u_i$  the initiation rate; and  $u_g$  the rate of chain growth.

When a polymer with a high degree of polymerization is produced, the rate of chain growth is incomparably higher than the rate of initiation, and  $u_g$  approaches the rate of polymerization  $u_p$ . At the beginning of the reaction  $[M^\bullet]$  increases, but since the rate at which radicals are consumed in the stage of chain termination is proportional to the square of the concentration of the radical, the rate of radical consumption quickly reaches the rate of their formation, i.e. the

concentration of the radicals reaches a steady-state value. For this condition

$$u_i = u_t = k_t [M^\bullet]^2 \quad (10.3)$$

It follows that the concentration of the polymer radicals will be

$$[M^\bullet] = \left[ \frac{u_i}{k_t} \right]^{1/2} \quad (10.4)$$

If (10.4) is substituted into equation (10.2), we obtain

$$u_p = -\frac{d[M]}{d\tau} = u_i + k_g [M] \left[ \frac{u_i}{k_t} \right]^{1/2} \quad (10.5)$$

Equation (10.2) can be rewritten with the value for the length of the kinetic chain  $\lambda$  substituted, where  $\lambda$  is the mean number of monomer molecules consumed in each act of initiation, i.e.  $\lambda = \frac{u_g}{u_i}$ . Then

$$u_p = -\frac{d[M]}{d\tau} = u_g \left( 1 + \frac{u_i}{u_g} \right) = u_g \left( 1 + \frac{1}{\lambda} \right) \quad (10.6)$$

From equations (10.2) and (10.4) it follows that

$$u_p = -\frac{d[M]}{d\tau} = k_g [M] [M^\bullet] \left( 1 + \frac{1}{\lambda} \right) = k_g [M] \left[ \frac{u_i}{k_t} \right]^{1/2} \left( 1 + \frac{1}{\lambda} \right) \quad (10.7)$$

If the degree of polymerization of the polymer formed is large enough, the  $\frac{1}{\lambda}$  value becomes very small and the expression enclosed in the round brackets approaches unity. For such a case, the polymerization rate of the system, which is equal to the rate of consumption of monomers in their reaction with the growing radical, will be

$$u_p = -\frac{d[M]}{d\tau} = k_g [M] \left[ \frac{u_i}{k_t} \right]^{1/2} \quad (10.8)$$

Since radicals originate by the process of initiation and end their existence when chain growth is terminated the rate of initiation is proportional to the concentration of the initiator,  $C_i$ , and at small values of  $C_i$

$$u_i = k_i [C_i] \quad (10.9)$$

The larger the amount of initiator present, the larger will the number of free radicals, which initiate the polymerization process, be that are formed per unit time. Then

$$u_p = -\frac{d[M]}{d\tau} = k_g [M] \left[ \frac{k_i}{k_t} \right]^{1/2} [C_i]^{1/2} \quad (10.10)$$

If we denote

$$k_g \left[ \frac{k_i}{k_t} \right]^{1/2} = k' \tag{10.11}$$

then

$$u_p = k' [M] [C_i]^{1/2} \tag{10.12}$$

If the logarithm of both sides of equation (10.12) is taken, it transforms to

$$\log u_p = \log k' [M] + \frac{1}{2} \log [C_i] \tag{10.13}$$

At high concentrations of the initiator, the dependence is much more complex. The values of the rate constants and activation energy [ $E_g$ ] of chain growth depend on the chemical nature of the monomer (Table 17).

TABLE 17

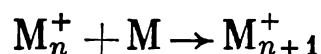
Rate Constants and Activation Energy for Monomers

Monomer	$k_g$ (at 60 °C)	$E_g$ (kJ/mole)
Acrylonitrile	1960	—
Butadiene	105	38.9
Vinylacetate	2040	17.6
Isoprene	50	41.0
Methylmetacrylate	575	19.6
Styrene	178	30.3
Vinyl chloride	12 900	15.5

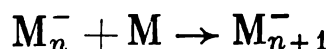
In industry for carrying out chain-polymerization processes, heating is employed together with the use of chemical agents—initiators or catalysts. The initiators (mainly compounds of a peroxide nature: organic peroxides, hydroperoxides and azocompounds) decompose in the course of the reaction to form reactive radicals, which enter into the polymer composition of molecules as chain end groups. The radicals of the initiator excite the monomer molecules; this results in formation of radicals of the monomers which unite with the radical chain. Consequently, radical polymerization always includes a stage of formation of free radicals followed by the growth of the polymer chain.

If the concentration of the initiator is raised, the number of free radicals formed by its decomposition grows and this increases the number of active centres and, as a result, leads to growth of the overall rate of polymerization and a drop in the mean molecular

weight (Fig. 94). In ionic polymerization (either of the cation or anion type), which occurs in the presence of a catalyst, the active, intermediate polymerization products are ions, ion pairs or polarized complexes. Ion polymerization can take place either by a chain or by a stepwise mechanism. In cationic polymerization the end of the growing chain is charged positively:



and in an anionic polymerization it is charged negatively:



The final stage of the polymerization process is chain termination, which occurs when polymer radicals become mutually saturated, when a free radical is saturated, or when a macromolecule is transformed into a stable compound by isomerization. Polymers obtained by the usual polymerization processes do not have an orderly spatial arrangement of the side groups along the axis of the macromolecule and this is the cause of the amorphous structure of such compounds.

The use of new complex catalysts, consisting of organometallic compounds (for example,  $Al(C_2H_5)_3$ ) or chlorides of metals with variable valencies (for example,  $TiCl_3$ ,  $TiCl_4$ ), has made it possible to obtain stereoregular polymers, with a strictly linear structure and symmetrical spatial orientation. Such polymers have higher strength and density and a higher melting point. Their macromolecules are easily oriented when the material is stretched and this results in a significant increase in the strength of the polymer in the direction of stretching.

Stereoregular polymers are usually produced by an anionic mechanism, and the process is carried out either by homogeneous or heterogeneous catalysis. In contrast to chain reactions in which low-molecular compounds are formed, in chain polymerization all the molecules which take part in the consecutive elementary acts of chain growth are joined by chemical bonds into one macromolecule. Both the length of the reaction chain and the molecular weight of the polymer depend on the ratio of the rates of the elementary reactions in the process of chain polymerization, i.e. the higher the rate of chain growth compared with the rate of chain-growth termination the larger will the length and weight of the chains be.

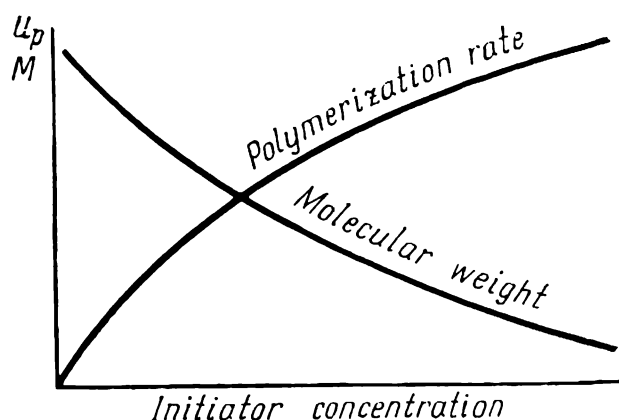


Fig. 94. The change in the rate of polymerization and in the molecular weight of a polymer with initiator concentration



Raising the temperature results in an increase in the number of elementary reactions of the polymerization process; it is accompanied by a considerable increase in the rate of formation of active centres. The increase in their concentration results in an increase in the rate of the reaction, and of chain growth, and especially in a sharp rise in the rate of chain-growth termination. Due to this, the mean molec-

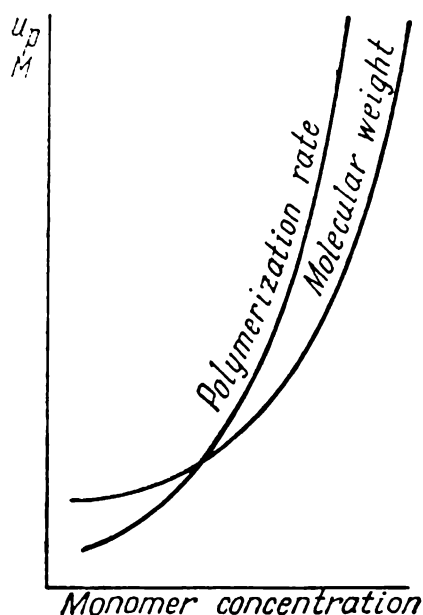


Fig. 95. The change in the rate of polymerization and in the molecular weight of a polymer with monomer concentration

ular weight of the polymer and the mean degree of polymerization drop. Moreover, if the temperature is raised, side reactions between functional groups of the monomer and of the polymer take place, and comparatively low-molecular polymerization products are formed.

High pressure significantly raises the rate of polymerization and this is not accompanied by a drop in the molecular weight of the polymer. The overall rate of polymerization carried out in a solvent and the molecular weight of the polymer grow with an increase in the concentration of the monomer (Fig. 95). If polymerization is carried out in a chemically inert solvent, which does not partici-

pate in the reaction, the dependence of the polymerization rate on the monomer concentration is given by the equation

$$u_p = kM^n \quad (10.14)$$

where  $n > 1$ .

Thus, the rate of the polymerization process and the mean molecular weight of the polymer produced depend on the temperature, pressure, activity of the catalyst or initiator, initiator concentration, presence of impurities, nature of the reaction medium, etc.

Impurities in the initial materials, depending on their nature, may accelerate, slow down or stop the polymerization process. In some cases the effects of foreign substances on the polymerization rate and on the properties of the polymers produced are utilized by adding to the monomers inhibitors: phenols, amines, quinones and other compounds. Chloroform, mercaptans and other compounds are sometimes used as regulators of the polymerization process—to promote the formation of a polymer with lower molecular weight.

The many methods used for carrying out polymerization can be divided into four kinds: (1) mass (bulk) polymerization; (2) solution polymerization; (3) emulsion polymerization; (4) bead polymerization.

In the **bulk-polymerization process** the monomer, a liquid or a gas, is introduced into a form (vessel) together with a catalyst or initiator (without a solvent) and then at a strictly controlled temperature most of the monomer is converted into a polymer in the shape of a block, tube, sheet, rod, or granules. The polymer body is then subjected to mechanical processing. Mass polymerization can be carried out either batchwise or as a continuous process. Whereas in the first stage of the process, in which active centres are formed, the monomer must be heated, later, when the chains are growing and heat is liberated, if necessary the reaction mixture is cooled. Since polymers are poor heat conductors, removal of the heat during the process from different points in the apparatus, especially from its centre, is not uniform and this results in non-uniform polymerization, i.e. in formation of products with different degrees of polymerization. Polystyrene, polymers of metacrylic acid, butadiene rubber and other polymers are made by this method from monomers, which contain practically no foreign substances.

In a continuous polymerization process a block is not produced, but the name "bulk polymerization" is still applied to polymerization of a pure monomer, to distinguish it from methods in which polymerization occurs in a solution of a monomer or its mixture with the medium.

In **solution polymerization** a solvent is selected in which both the monomer and the polymer formed are soluble, or one in which only the monomer is soluble, and the polymer is precipitated as it is formed. In the first case the solution is a ready to use varnish, and this method is often employed in the paint- and varnish-manufacturing industry. In the second case, the polymer precipitate, which is in the form of finely divided particles, is filtered off, washed and dried.

In a solution polymerization process the monomer, the catalyst, initiator and other admixtures are all dissolved in the liquid selected and the solution is heated in a reactor with a stirrer under active agitation. Heat is removed from the reaction zone and the temperature is controlled by means of a coil or a water jacket which makes the thermal regime of the process much better than that of the bulk method. Polymers obtained in this way are more uniform in structure, but usually have a lower molecular weight than those made using other methods since chain growth is quickly terminated due to the influence of the molecules of the solvent. This method is employed, for example, in making vinylacetylene polymers in methyl alcohol.

**Emulsion polymerization** is the most commonly used method at present. In this method the monomer, a water-soluble initiator, stabilizer and other admixtures are dispersed in water or an aqueous solution of salts in the presence of an emulsifying agent and under

intensive agitation they form an emulsion. The water, which is the dispersion medium, must be carefully purified to remove impurities that may affect the stability of the emulsion or the course of the polymerization process. The rate of the process is higher than in bulk polymerization and the polymer formed has the highest molecular weight.

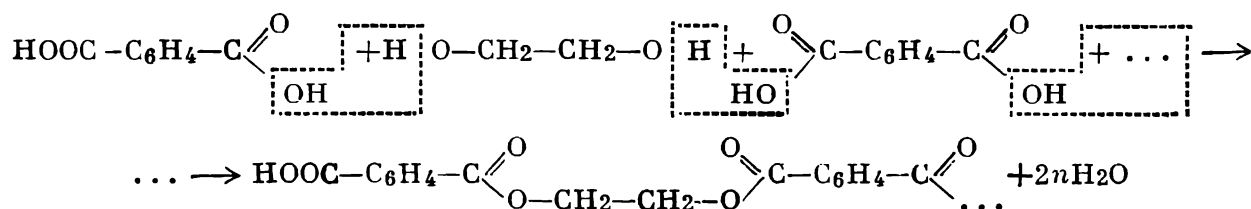
The reaction mixture consists, as a rule, of a large number of components: the liquid monomer (15-30 per cent of the mass of the entire mixture), water (60-80 per cent), emulgator, an initiator soluble in water and agents which control the pH of the medium, surface tension, degree of polymerization and polymer branching. The pH of the medium affects the polymerization rate and the quality and yield of the polymer formed. The kinetics of the process and the degree of polymerization of the polymer formed depend also on the temperature and the duration of the process, the quantity of the initiator used, the amount and nature of the emulgator, the intensity of agitation and other factors. When a polymer with the necessary properties is obtained, an acid or other electrolyte is added to destroy the emulsion.

A negative feature of the process is contamination of the polymer with the emulgators, which lowers the quality of the fabricated wares. Polyvinylchloride, some grades of polystyrene and many copolymers of butadiene, vinylacetate, acrylonitrile, etc. are manufactured by this method.

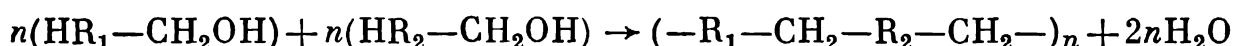
In **bead polymerization** also known as **suspension polymerization**, the initiators used are insoluble in water, but soluble in the monomer. Large drops of the monomer are produced—from 0.05 to 0.3 cm in diameter, whereas the particles of the emulsions are from  $10^{-3}$  to  $10^{-4}$  cm in size and this greatly simplifies separation and purification of the polymer formed without reducing the rate of the operation. Polymerization takes place independently in each drop, which is a sort of monomer "reservoir", and this promotes good removal of the heat developed. The polymer, which has a high molecular weight, is precipitated in the form of water-insoluble solid particles.

**Polycondensation** is a process in which the reaction between a large number of molecules of two or more different monomers is accompanied by liberation of a corresponding amount of low-molecular by-products, for example, water or alcohol. The presence of these products makes the process reversible. The elementary composition of the high-molecular compound produced differs from the composition of the initial monomers, the molecular weight of the substance grows continuously during the course of the reaction. Functional groups of the molecules—COOH, OH,  $\text{NH}_2$ , etc., are usually involved in the reaction. Phenolformaldehyde resins, urea-formaldehyde resins, nylon, terylene, enant, etc. are made by such reactions. The resin terylene, for instance, is produced from ethyl-

ene glycol and terephthalic acid:



or in the usual form:



Depending on the method by which the reaction is carried out and on the molecular structure of the initial monomers, polycondensation can be an equilibrium, or an irreversible reaction. Irreversible polycondensation usually takes place at a very high rate. Reversible polycondensation, as a rule, proceeds at a low rate. Polyamides are made from diamines and dicarbonic acids in this way.

A reversible polycondensation process, just as ordinary condensation, is described by the equilibrium constant  $K$  and rate constants of the forward and reverse reactions. At equilibrium the rate of formation of the high-molecular compound is the same as its rate of decomposition. If both reactions are of the second order and it is arbitrarily assumed that the functional groups take part only in polycondensation reactions and do not take part in side reactions, then the actual rate of formation of the polycondensation product,  $u$ , at time  $\tau$  will be:

$$u = \vec{u}_1 - \overleftarrow{u}_2 = k_1(1 - \varphi_\tau)^2 = k_2\varphi_\tau G \quad (10.15)$$

where  $\vec{u}_1$  and  $\overleftarrow{u}_2$  are the rates of polycondensation and the reverse reaction, decomposition, and  $k_1$  and  $k_2$  the velocity constants of the polycondensation and the reverse reactions;  $\varphi_\tau$  the number of functional groups of the initial compound which have entered into the polycondensation reaction at time  $\tau$  (the total content of functional groups in the initial mixture was taken as unity and, therefore,  $\varphi_\tau$  is a fraction of 1);  $G$  the amount of the low-molecular product formed at time  $\tau$ .

The equilibrium constant of a reversible reaction is  $K = \frac{k_1}{k_2}$ . Consequently, the actual rate of formation of high-molecular compounds by a process of polycondensation can be expressed as

$$u = k_1 \left[ (1 - \varphi_\tau)^2 - \frac{\varphi_\tau G}{K} \right] \quad (10.16)$$

From equation (10.16) it can be seen that the rate of the polycondensation process, the equilibrium conditions and the yield of the end high-molecular product depend to a very large extent on the quantity of the low-molecular by-product  $G$  present in the reaction

medium. The dependence of the maximum polycondensation degree,  $\bar{x}_p$ , on the equilibrium constant,  $K$ , and the concentration of the low-molecular compound in the reaction mixture,  $C$  is expressed by the polycondensation equilibrium equation

$$\bar{x}_p = \sqrt{\frac{K}{C}} \quad (10.17)$$

and is given in Fig. 96. It follows, according to equation (10.17), that to obtain a polymer with high molecular weight, maximum separation of the low-molecular compound from the reaction zone is necessary.

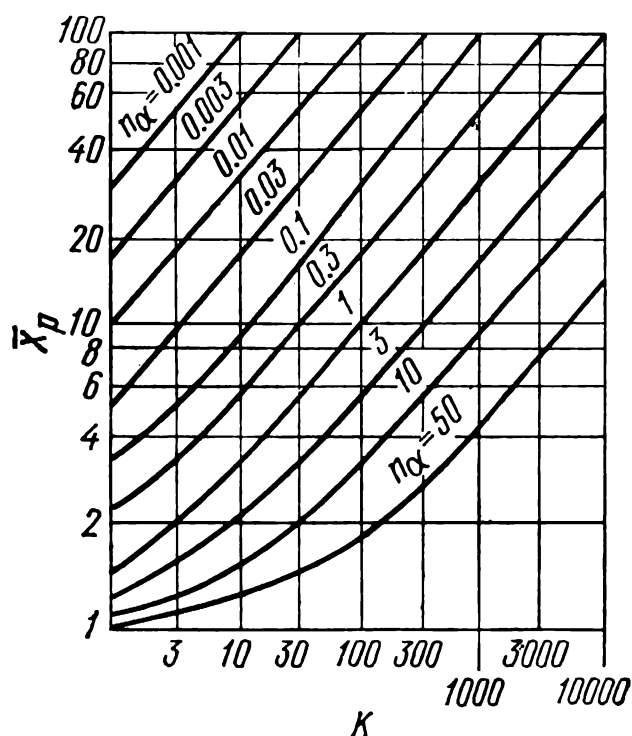


Fig. 96. Polycondensation degree as a function of the equilibrium constant for different contents of the low-molecular compound which separates off (logarithmic scale)

If all the side components formed were immediately removed from the reaction zone in the course of the reaction, the degree of polycondensation would continuously and uniformly increase.

The viscosity of the reaction mixture increases with growth of the molecular weight of the basic end product, the mobility of the macromolecules formed is reduced (and consequently, the number of their collisions) and the removal of the side products simultaneously becomes more difficult. These and some other factors (approach to equilibrium, changes in the structure of functional groups, etc.) may bring the polycondensation process to an end. To prevent

the process from dying down, the temperature of the reaction mixture must be raised; this lowers the viscosity of the medium and to a certain degree increases the rate of diffusion of the low-molecular by-products formed to the phase interface.

It should be remembered however, that when a certain, limiting value is reached, high temperature may result in destruction of the initial substances or of intermediate compounds formed in the course of polycondensation (even if there is a corresponding drop in the pressure in the reactor) or even in partial separation from the reaction zone of the more volatile, unreacted component and this in turn, according to the Le Chatelier principle, will lead to a shift of the reaction equilibrium in the opposite direction, and to a reduction in the molecular weight of the products formed. The lower the temperature the higher will the molecular weight at equilibrium be.

Therefore, the first stages of polycondensation are carried out at high temperatures to achieve a high process rate, and the temperature is then decreased as equilibrium is approached so as to obtain a product of high molecular mass.

The dependence of the degree of polymerization  $n$  on the conversion  $x$  and the number of functional groups  $N$  is expressed by the formula

$$n = \frac{2}{2 - xN} \quad (10.18)$$

Since two functional groups participate in each stage of polycondensation, the conclusion can be drawn that the process is governed by a second-order kinetics equation, which, at equal concentrations of each of the functional groups, can be written as

$$-\frac{dC}{d\tau} = kC^2 \quad \text{or} \quad \frac{dC}{C^2} = k d\tau \quad (10.19)$$

and after integration

$$\frac{1}{C} = k\tau + \text{const} \quad (10.20)$$

Since the concentration of the reacting components is directly proportional to the sum of their molecules  $N$  at time  $\tau$ , equation (10.20) transforms into

$$\frac{1}{N} = k'\tau + \text{const} \quad (10.21)$$

Inasmuch as the number of molecules  $N$  present at time  $\tau$  is related to the number of molecules  $N_0$  in the initial reaction mixture by

$$N_0 = Nn \quad (10.22)$$

then

$$N = \frac{N_0}{n}$$

and equation (10.21) transforms into

$$\frac{n}{N_0} = k'\tau + \text{const} \quad (10.23)$$

Consequently, the mean degree of polymerization  $n$  is directly proportional to the time, and this is confirmed by experimental data (Fig. 97). The dependence of the rate constant on the polycondensation temperature is described by the Arrhenius equation (Fig. 98). The polycondensation processes follow a stepwise pattern. Chain growth proceeds gradually, by interaction of the monomer molecules with the polymer already formed. At definite stages of the process the molecules have a linear or a branched structure and only in the final stage of end product formation do reactions take place which

produce a three-dimensional structure. The basic factors on which the rate and direction of the polycondensation reaction depend are the structure of the monomers, in particular the number of functional groups in them, their properties and content in the reaction mixture, the type of catalyst used and its activity, the presence of impurities in the monomer, and also strict control of the regime parameters (temperature, pressure, intensity of agitation, process duration, etc.). Impurities present lower the molecular weight, form inactive end groups and cause branching of the macromolecules.

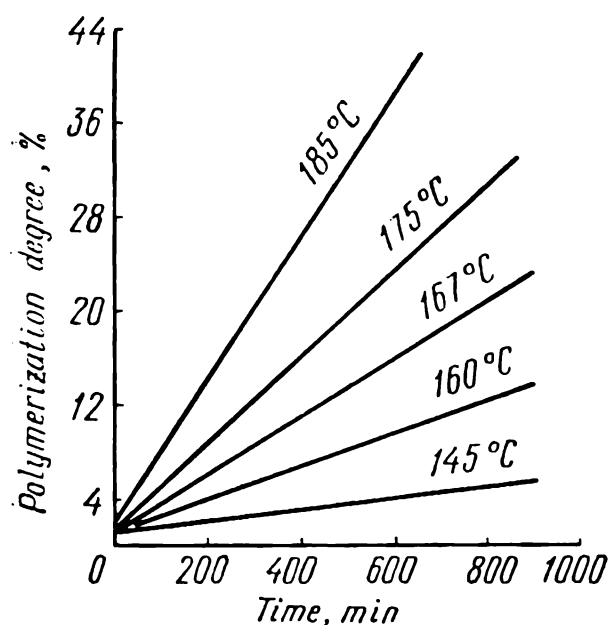


Fig. 97. Polymerization degree as a function of reaction time (the kinetics of the polycondensation of hexamethylenediamine and sebacic acid) at different temperatures

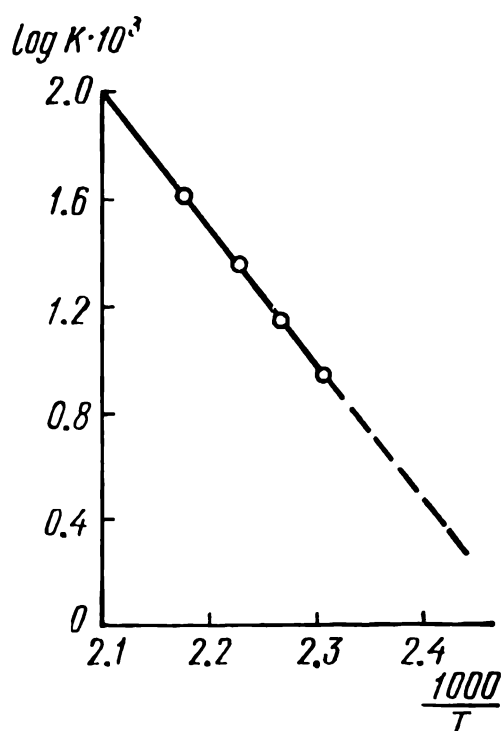


Fig. 98. Logarithm of rate-constant for polycondensation of hexamethylenediamine and sebacic acid as a function of the inverse temperature ( $E = 24$  kcal per mole)

Polycondensation is carried out in a melt, in solution or at the phase interface. In this last process of heterogeneous polycondensation, the reaction rate is very high. Various methods of polycondensation are employed to produce polyamides, polyesters, polyurethanes, polycarbonates, and some other polymers.

New polymer materials can be developed more easily and at lower cost by modifying existing polymers. The following methods of modification are employed in industry: (1) changing the chemical structure of the polymer macromolecules (chemical modification); (2) changing the physical structure of the polymer without a change in its molecular weight and chemical structure (structural modification); (3) employing mixtures of the polymer with other compounds.

Chemical modification is the most extensively used; it is carried out by introducing new functional groups into the polymer mole-

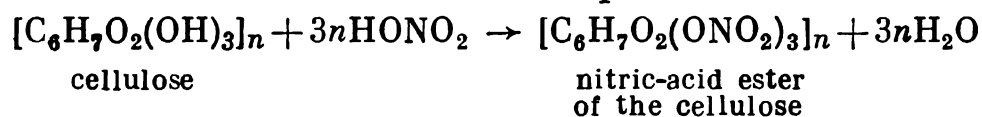
cule, introducing new links in the macromolecule (copolymer synthesis) or forming grafted and bulk copolymers and also branched and stereopolymers.

The physical and chemical properties of a polymer are to a very large extent determined by the nature of the functional groups and their properties, and also by the size and structure of the macromolecules. There are four types of chemical reactions which are characteristic for high-molecular compounds:

1. Formation of three-dimensional molecules by means of chemical links between chains—cross-linked polymerization (for example, vulcanization of rubber and tanning of leather).

2. Splitting up chain molecules into shorter ones (destruction) under the effect of light radiation, thermal, mechanical or chemical factors. Generally, such destruction leads to formation of elementary substances. The decrease in the molecular weight reduces elasticity and tensile and bending strength, changes the viscosity of solutions, etc. Destruction is utilized in making plasticates, rubber, casting compositions, etc.

3. Substitution of other groups or atoms for side functional groups of the macromolecules by means of a reaction with low-molecular compounds. Thus, from cellulose, which contains three hydroxyl groups in each of its elementary links, a number of esters are obtained. Nitration of cellulose can be represented as follows:



The basic chain of the high-molecular compound is not changed by the reaction. The rate of reactions of this type in most cases depends on the rate of diffusion of the low-molecular compound into the polymer phase.

4. Intramolecular reactions, which take place between functional groups of one and the same macromolecule (intramolecular ring formation).

### 3. The Manufacture and Uses of Cellulose

Cellulose is one of the principal polymer materials.

Cellulose has a fibrous structure; it is the principal component of the covering of vegetable cells; the hard skeleton of all plants is made of cellulose and accompanying substances (incrustations). In the most pure form cellulose is contained in cotton fibre (up to 96-98 per cent), whereas wood along with cellulose also contains large amounts of other organic substances: hemicelluloses, lignin, tars, fats, proteins, and dyes. The fraction of the mineral substances in it amounts to only 0.3-1.1 per cent.

An analysis of the elementary composition of wood shows that on the average absolutely dry wood contains approximately 50 per cent



carbon, 6.3 per cent hydrogen, 43.6 per cent oxygen and 0.1-0.2 per cent nitrogen. Dry wood contains from 40 to 60 per cent of so-called  $\alpha$ -cellulose, i.e. cellulose insoluble in a 17.5-18 per cent aqueous sodium-hydroxide solution at room temperatures.

Cellulose is a high-molecular polysaccharide with a large and complex molecular chain containing thousands of elementary links. Its molecules have a regular, absolutely linear structure. The molecular weight of technical-grade cellulose varies between 50 000 to 150 000, and even higher. The cellulose imparts mechanical strength and elasticity to vegetable tissues, forming something like a plant skeleton.

**Hemicelluloses** are polysaccharides (hexosans, pentosans, polyuronic acids) which accompany the cellulose, but differ from it in having shorter chains and lower chemical stability. Hemicellulose hydrolyzes more readily and is transferred to the solution in dilute mineral acids and alkalies. Hexosans yield hexose—sugars which can be fermented to form alcohol. The hemicellulose content of wood depends very strongly on its kind, thus in soft wood the content amounts to 17-20 per cent, and in hard wood to 30-35 per cent. This is taken into consideration in selecting the technological regime.

**Lignin** is a complex mixture of organic substances of aromatic nature which contains larger amounts of carbon than cellulose (61-65 per cent); the hardness and resilience of the cell walls are due to the lignin present in them. Compared with other wood components, lignin is more reactive, and it easily changes when acted upon with hot alkalies, oxidizing agents, etc. The lignin content of wood lies between 17 and 30 per cent.

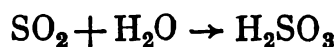
The manufacture of pulp from wood is based on its high stability toward certain chemical compounds, which under proper conditions transfer the accompanying, less stable substances (lignin, hemicellulose, etc.) to solution. Depending on the substances used, the processes for manufacturing pulp can be divided into three basic groups: acid, alkali and combined processes. At present, the processes employed commercially are: the sulphite processes, sulphate processes, sulphate process with preliminary acid- or aqueous hydrolysis of the wood, sulphite-alkali, nitric-alkali and some others. The first two methods are used most extensively.

The basic stages of all technological processes for making wood pulp are: (1) preliminary processing of the wood; (2) preparation of the cooking liquor; (3) digestion of the wood lignin; and (4) processing the pulp obtained by purifying, sorting, dehydration, pressing, cutting into sheets and sometimes finishing, refining and bleaching it. The quality of the pulp depends not only on the manufacturing method, but also on the kind of wood used, its age, the density and moisture-content of the wood, presence of rot, knots and other faults.

Although pulp can be produced from any type of wood, up to the present predominantly low-tar-content kinds have been used, such as spruce, fir, and beech which can be processed by any of the digestion methods. The tarry kinds (pine) are mainly processed by alkaline methods. The fibre of pulp made from pine wood is shorter than that from spruce. Hardwood contains very large amounts of pentosans, and its fibres are very short. To obtain high-quality cellulose, the pulp wood processed must be sorted out, uniform, mature and cut into pieces of standard lengths (from 0.75 to 3.2 m).

**Preparation of the wood** consists in removing the bark, knots and rot from the pulp wood and in disintegrating it in chopping machines into chips 15-30 mm long and up to 3 mm thick. To prepare the digester acid used in the sulphite manufacturing method furnace gas obtained by roasting pyrites or burning sulphur is purified to remove selenium, arsenic,  $\text{SO}_3$ , dust, unburnt sulphur, etc., which, when present, disrupt the normal course of digestion and lower pulp quality. Selenium is an especially harmful impurity—it is a catalyst for the oxidation of bisulphite solutions; it causes conversion of  $\text{SO}_3^{2-}$  into  $\text{SO}_4^{2-}$ . The content of selenium in the raw material should therefore not exceed 0.012 per cent for pyrite and 0.03 per cent for sulphur.

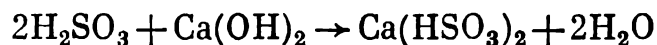
The purified gas, cooled to 30-35 °C, is passed through high towers filled with limestone and sprayed with water. The  $\text{SO}_2$  is absorbed and a solution of sulphurous acid is formed



which reacts with the limestone to produce a calcium bisulphite solution:



In towers of another type milk of lime is used:



The digester acid produced is in addition saturated with sulphurous anhydride utilizing purge gases which are discharged during the digestion process. Digester acid made in this way contains excess sulphur dioxide (from 3 to 6 per cent free  $\text{SO}_2$  and approximately 2 per cent  $\text{SO}_2$  in the form of the bisulphite of calcium, magnesium, sodium or ammonium).

**Cellulose digestion** is carried out in large steel digesters (Fig. 99) with capacities of 340 m<sup>3</sup> and more (12-16 m high and 5-6.5 m in diameter at the cylindrical part). The digesters are lined with acid-resistant concrete covered with acid-resistant ceramic slabs fixed by means of a special cement. The overall thickness of the lining is 170-180 mm. In recent years bimetal digesters are also being employed. A thin layer of acid-resistant steel is joined to a sheet of

a carbon steel by hot rolling as a protective layer against corrosion by the cooking liquor.

The digester operates batchwise. A complete cycle lasts from 6 to 12 hours and consists of the following operations: (1) filling the digester with chips and acid; (2) digesting; (3) discharging the gas and liquor from the vessel; (4) unloading the digester. After the vessel has been filled with chips through the throat at the top, 0.6-0.7 m<sup>3</sup> of the digester acid per cu m of vessel volume is introduced

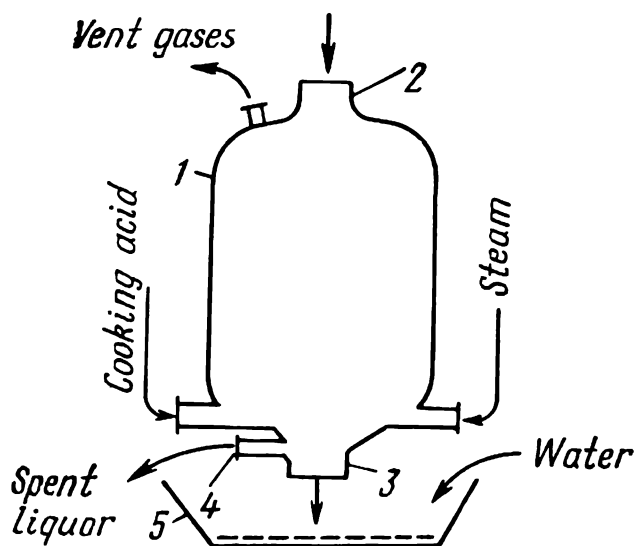


Fig. 99. Schematic diagram of a wood-pulp digester:

1—digester shell; 2—charging opening for the wood chips; 3—blow pipe; 4—pipe for spent-liquor discharge; 5—blow pit

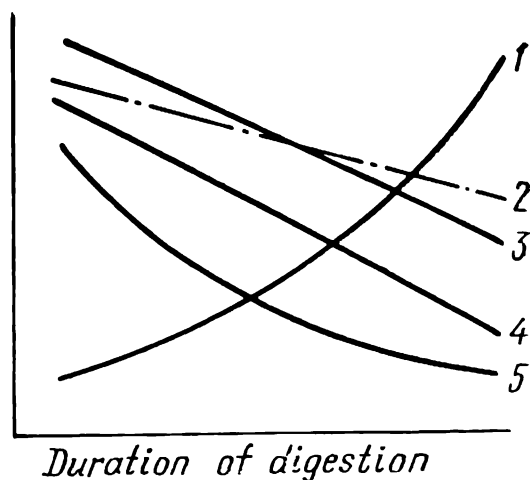


Fig. 100. The change in the composition of the wood and in the degree of polymerization in the course of digestion:

1—cellulose; 2—pentosans; 3—lignin; 4—degree of polymerization of the cellulose; 5—cellulose yield

through a nipple at the bottom. The digester acid impregnates the chips. The acid also displaces the air contained in the digester and in the chips. Following this, digestion begins—the contents of the vessel are heated with live steam introduced through the nipple at the bottom.

The aim of the digestion operation is to achieve maximum removal of all impurities (lignin, hemicellulose, etc.) to the solution, leaving cellulose as an unchanged residue. At 105-110 °C the chips settle, the steam penetrates into them, and they are impregnated with the digester acid, which diffuses deep into the chips. Sulphur dioxide and bisulphite contained in the digester acid react with the lignin, and at 70 °C active liginosulphonic acid and its calcium, magnesium, sodium or ammonium salts begin to form. The temperature is gradually raised to 135-147 °C (a pressure of 5-7 atm). The calcium, or other, salts of liginosulphonic acid are transferred to the solution. A large part of the hemicellulose is also hydrolyzed and dissolved; as a result, the sugar content of the liquor is significantly increased.

The reaction of lignin with sulphurous acid and bisulphite is a heterogeneous oxidation-reduction process occurring gradually and involving the oxidation of  $\text{SO}_3^{2-}$  to  $\text{SO}_4^{2-}$  and reduction of lignin by intermolecular regrouping.

The delignification rate is proportional to the excess of  $\text{SO}_2$  in the cooking liquor and it approximately doubles with each  $10^\circ\text{C}$  increase in the temperature. The change in the content of wood components, including that of the cellulose, its yield and degree of polymerization during the digestion are shown in Fig. 100.

The amount of lignin remaining after digestion is the criterion for determining the quality of the cellulose produced. If there is more than 3 per cent residual lignin, the cellulose is graded as hard, if there is less than 2 per cent, the cellulose is considered soft. The duration of digestion, the yield and quality of the pulp produced, specific consumption of steam and sulphur depend on the properties of the raw material, the rate at which the temperature in the vessel is raised, the pressure and the composition of the digester acid. Rapid heating and a high final temperature accelerate digestion, but produce lower-quality pulp. The best method for intensifying the process is, therefore, the use of acid with higher  $\text{SO}_2$  and calcium bisulphite concentrations. Forced circulation of the acid through the digester during cooking is used to provide uniform heating and better impregnation of the chips: the digester acid is withdrawn with an acid-resistant pump, passed through a heater and repumped to the vessel.

Periodically during the course of the digesting process gases and vapours formed are purged and unreacted sulphur dioxide is absorbed and utilized for strengthening the digester acid. When digestion is completed the pressure in the vessel is lowered to 2-4 atm by releasing the gas-vapour mixture, and all the contents of the vessel are blown out through a large-diameter discharge to a blow pit. This lasts 8 to 12 minutes. At some plants the digester contents are washed to the blow pit with water.

The washed pulp is diluted with water to a concentration of 1-1.2 per cent and pumped to the purification section, where knots, undigested chips and mineral impurities are removed from the fibre by passing it through the grating of a knot-removal filter, a riffer-settling tank and, finally, through grading sieves.

Pulp intended for chemical processing and for making white paper is subjected to bleaching and refining. Refining is accomplished by processing the pulp at a low temperature of about  $20^\circ\text{C}$  with a 12 per cent sodium hydroxide solution or by boiling it in a solution containing about 1 per cent  $\text{NaOH}$ . During bleaching and refining a large part of the lignin, ash, hemicellulose, tarry substances and products of cellulose decomposition, which remain in the pulp after digestion, are transferred to solution; the content of the principal

component,  $\alpha$ -cellulose, is raised to 92-97 per cent and the pulp becomes more uniform. At the same time, the pulp acquires such properties important for chemical processing as swelling, increased reactivity and more uniform viscosity.

After this, the wood pulp is carefully washed with water to remove chlorine and acidic substances, then dehydrated to a water content of 6 to 12 per cent, and formed into a wide, continuous ribbon, which is cut into sheets ( $600 \times 800$  mm) and packed.

The use of new methods for manufacturing pulp, i.e. digesting the wood employing soluble (ammonia and sodium) and semisoluble (magnesium) bases, has raised digester capacities from 10 to 15 per cent, and increased the yield and strength of the pulp produced. The use of soluble bases has made it possible to carry out digestion not only in acidic and neutral, but also in alkaline media, in several stages and to obtain different grades of pulp from diverse raw materials.

**The sulphate method** of making pulp, in which the chips are digested in an alkaline solution ( $\text{NaOH} + \text{Na}_2\text{S}$ ), has extended the raw-material base of the industry, since this method can be used to process any kind of wood, including waste products of saw-mills and wood-working plants. The well-developed system for regenerating the spent liquor and consequent returning its components to the manufacturing process reduces stream pollution to a minimum; pollution is relatively larger in making sulphite pulp.

In recent years **continuous digesting** is coming into wide use. The apparatus employed for this, which consists of a digester or tube, with provisions for continuous feeding of the raw materials and unloading of the pulp produced, has a production capacity of 300-400 tons of cellulose per day. The digesters, depending on the residence time of the raw material in them, can be divided into two groups: units in which the time is up to 4 hours, and units with rapid digesting (up to 1 hour). Fig. 101 shows a multitube unit, which can have from two to eight tubes, 6-10 m long and from 300 to 1200 mm in diameter. The worm-screw conveyer in each tube moves the mixture through the tubes. The liquor and steam consumed in the digesting process are fed through nozzles located in the upper part of the first and second digesting tubes. The digesting conditions are: a pressure of up to 12 atm, and a temperature of 170-190 °C. The digester operates at roughly plug flow.

The manufacture of ground wood is continuously growing, and this material is successfully being used for making paper and cardboard of various grades. Ordinary ground wood is made by mechanical attrition of wood in the presence of water by means of stone cylinders with a rough surface, known as defibrators.

Semichemical ground wood is produced from logs impregnated with chemicals and then subjected to attrition in a defibrator or

from impregnated chips by disintegrating them in refiners of various types. The yield of this pulp is approximately 85 per cent and its strength is 2-3 times that of ordinary ground wood.

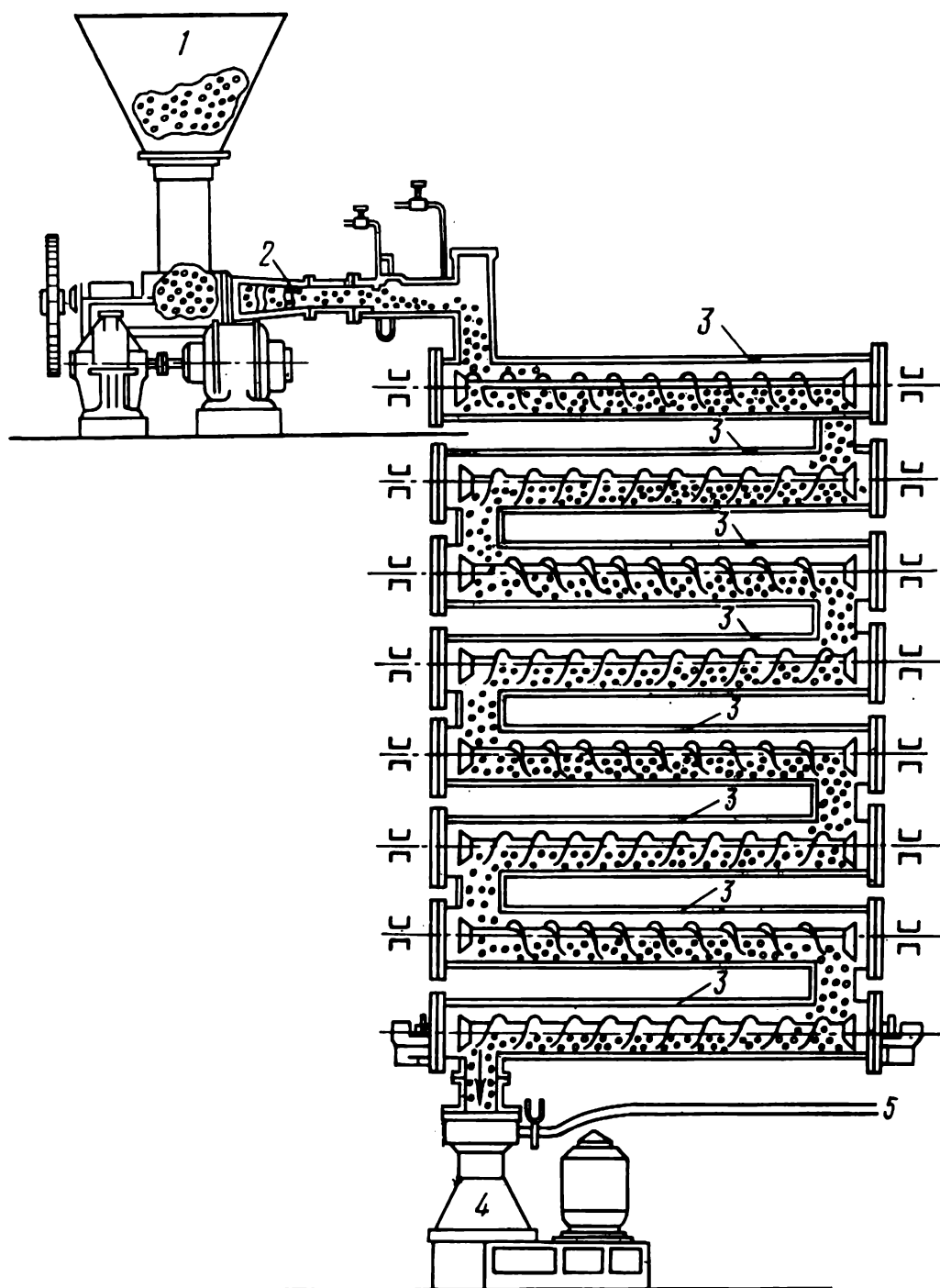


Fig. 101. Tubular digester unit:

1—hopper; 2—worm feeder; 3—digester tubes with worms; 4—discharge mechanism; 5—venting pipe

Cellulose manufacturing can advantageously be combined with electrochemical manufacturing of chlorine and sodium hydroxide.

Utilization of the gases and liquors produced in manufacturing wood pulp by the sulphite method is an important factor. A mixture of cymene and terpenic hydrocarbons is recovered from the gases to

form so-called "sulphite oil". Then  $\text{SO}_2$  liberated in the digesters is absorbed by digester acid. The spent sulphite liquor, which is separated from the pulp at the end of the digestion operation in the amount of 10-12 tons per ton pulp produced, contains more than 50 per cent of the organic substances of the initial wood—lignosulphonic acids with various degrees of sulphonation and polymerization, sugars—products of hemicellulose hydrolysis, formic and acetic acids, cymene, furfural, etc. About 65 per cent of the saccharides (hexoses) contained in the liquor after its neutralization are utilized in making ethyl alcohol by its fermentation in the presence of yeast:



From 80 to 90 litres of alcohols per ton cellulose can be obtained from the weak liquor produced in this way. The solution remaining after the alcohol has been distilled off contains unfermented pentose saccharides, from which fodder yeast can be made. The spent liquor, evaporated to a 50% concentration, is used for making foundry binders. The spent-liquor concentrates are also utilized in the petroleum industry, in making plasticized cement, sand-lime brick, in ore-agglomeration and flotation processes, in making abrasive disks, foundry paints which prevent formation of faults in castings, detergents, fuel briquettes, electrodes, insulation board, etc.

The lignosulphonic fraction of the liquor can be utilized for making tanning extracts and vanillin. The dry residue of the sulphite liquor is employed as a fuel. However these methods do not provide integral utilization of the liquors produced in pulping wood. Large amounts of the liquors are discharged into lakes and streams, and they must first be processed to prevent them from damaging vegetable and animal life.

Chemical pulp and pulp are used in making paper and cardboard, artificial fibres, plastics, lacquers, film, smokeless powder, etc. For making paper the fibre, mixed with water and with other components according to the formulation being used, is poured onto the moving, endless sieve of a paper-making machine. The water is removed through the sieve holes and a layer of interwoven fibres is produced—a paper sheet from which remaining water is first pressed out, after which it is dried. To obtain a sheet with uniformly interwoven fibres, the pulp is preliminarily subjected to grinding. High-grade paper is made from pure, bleached pulp whereas paperprint contains 25 per cent unbleached pulp and 75 per cent ground wood.

Cellulose, which does not itself possess plastic properties, cannot serve as a binder and, therefore, for making plastics cellulose esters are manufactured—they exhibit plasticity under certain conditions. Cellulose reacts with acids to form esters: nitrate-, acetate-, etc. But cellulose, in the same fashion as other alcohols, can also form ethers such as ethylcellulose, benzylcellulose, etc.

#### 4. The Manufacture of Chemical Fibres

Fibres have a length many times larger than their very small diameter, which is usually measured in microns. Fibrous materials, i.e. substances composed of fibres, are extensively used. Diverse textile goods, furs, leathers, paper, etc. are examples.

Almost up to the beginning of the 20th century only natural fibrous materials such as cotton, wool, flax, natural silk, hemp, and jute were used for making fibre and cloths from the fibres. However, these did not fully satisfy all the requirements both with respect to amounts available and properties of the materials. This led to development of methods for making artificial and synthetic fibres.

According to their origin, all fibres can be divided into natural and chemical ones. The latter in turn can be divided into artificial fibres, made from high-molecular compounds which are present in nature in their ready form (cellulose, casein, etc.) and synthetic fibres, made of high-molecular compounds synthesized from monomers.

The use of chemical fibres is continuously growing. Their wide use results from the economic advantages of manufacturing and employing them, the fact that production does not depend on the weather and soil conditions, the practically inexhaustible resources of raw material and because fibres with entirely new and very valuable properties can be made. Thus, manpower expenditures (days) for producing one ton of fibre are: for wool (washed)—400, and for cotton—238, whereas for viscose-staple fibre the figure is only 50.

Whereas natural fibres do not differ very sharply in their properties, chemical fibres can possess a complex of prescribed properties, depending on their application. Chemical fibres are used for making cloth, knit ware, fur, clothes, shoes, upholstery, sporting goods, haberdashery, draperies, brushes, lapel cloth, synthetic leather and also such industrial items as tire cord, filter cloth, upholstery for cars, fishing equipment which does not rot in water, ropes, sail cloth, parachutes, balloons, pressure suits, artificial bristle, electrical insulating materials, belt-drives, high-strength canvas, fire hoses, pipes, conveyer belts, surgical thread, various types of industrial clothing, etc. Chemical fibres are used in sealing apparatus operating in chemically-corrosive atmospheres.

There is much in common in the methods used for making diverse chemical fibres from natural polymers and from synthetic resins, although each of the methods may possess its peculiar specific features.

Irrespective of the nature of the raw material, the flow scheme of the overall process used for making a chemical fibre can be divided into four stages.



1. Production of the initial material (the intermediate product). When the raw material is a natural high-molecular compound, the impurities must first be removed. When it is a synthetic fibre, the initial stage consists in the synthesis of the polymers—manufacture of the resins.

In spite of their diversity, the initial polymer materials must all meet the following, common, requirements, for a fibre to be formed from it and for it to have sufficient strength: (1) the molecules must have a linear structure, so that the initial material can be dissolved or melted for the formation of the fibre and for orientation of the molecules in the fibre; (2) the molecular weight must lie within definite limits (usually between 15 000 and 100 000), since if the molecules are too small the necessary fibre strength is not obtained, and if they are too large it is difficult to form a fibre, due to the low mobility of the molecules; (3) the polymer must be pure, since impurities, as a rule, sharply reduce fibre strength.

2. Preparation of the spinning body. Not all natural and synthetic high polymers can be used for making fibres. Viscous, concentrated solutions (7-25 per cent) of high polymers in available solvents (alkali, acetone, alcohol, etc.) must be prepared or resins be transformed to the molten state for spinning, or more properly, formation of chemical fibres to be possible. Only in a solution or in the molten material are the conditions obtained for lowering the energy of interaction between macromolecules and, after the intermolecular bonds have been broken, for orientation of the molecules along the axis of the fibre being formed. Cellulose, for example, is transferred to solution using chemical reagents. Some resins dissolve in acetone or melt when the temperature is raised. The solution or melt is carefully purified by filtering it 2-4 times and removing air bubbles. During this stage dyes and other reagents are added to give the fibre its colour, lustrelessness, etc.

3. Formation of the fibre is the most important operation. It is accomplished by passing the material through a spinneret (thread former) which has a large number of tiny openings (from 100 to 6000, depending on the spinning process) in its bottom.

In recent years the holes in the spinneret are often made not round, but triangular or star-shaped. This produces special profile fibres with large adherence between filaments. Wares made of such fibres have excellent wearing properties. Fine streams of the solution are forced through spinneret openings into a settling bath, where the polymer precipitates from the solution by chemical reactions, i.e. the streams solidify and each of them forms an elementary filament. This is the method of wet spinning from solution, used in making viscose and cuprammonium fibres. If solidification occurs in a stream of hot air which evaporates a volatile solvent (recycled in the process), the process is called dry spinning from solution. Acetate fibre as well

as some other kinds of synthetic fibres are made by this method. Solidification can also take place in a stream of cold air—this is known as dry spinning from a melt (capron, nylon). It follows from the above, that the method used to solidify a fibre depends on the kind of the material from which it is made.

The bundles of fine filaments formed by the streams are continuously directed to a receiving device by guides and then stretched (formation is carried out under tension) by the coiling devices—the bobbin, roller, centrifuge. In the formation process the linear macromolecules are oriented along the axis of the fibre (Fig. 102). The prop-

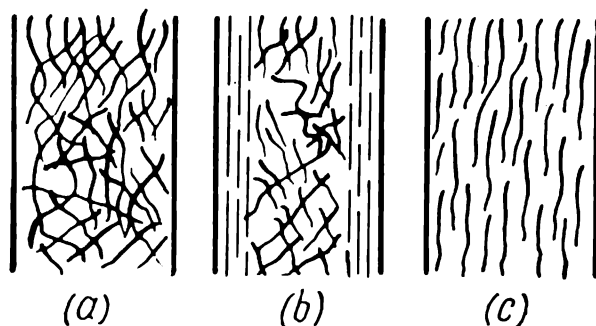


Fig. 102. Orientation of linear macromolecules during fibre formation:  
(a)—molecules in state of disorder; (b)—partial orientation; (c)—orientation

erties of the fibre can be changed by varying the conditions of formation and stretching since stretching affects the structure and the strength of the fibre.

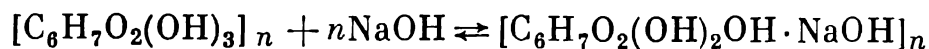
Chemical fibres, independent of the fabrication method, can be obtained either in the form of an endless silk thread or in the form of staple fibres (short cuttings, 30 to 150 mm long). The silk thread is directly used at textile or knit-goods plants, whereas the staple fibre is reprocessed into yarn, either from pure staple or from its mixture with other fibres.

4. The finishing operations give the fibre the properties necessary for further processing. The fibre is carefully washed to remove all impurities introduced during fibre formation and in preceding chemical processes. Besides this the fibre is bleached and in some cases dyed, and it is made slippery by applying soap or some fat-containing solution, so as to make processing at the textile plants easier. After the silk has been dried, it is twisted and rolled onto spools or bobbins; staple fibres are packed in bales.

**The viscose process** for making artificial fibres from cellulose is most widely used. Production of viscose fibres, in the form of artificial silk, tire cord and staple, amounts to approximately 70 per cent of total chemical fibre production.

To prepare the spinning solution, cellulose with a 5-6 per cent moisture content, ordinarily in  $600 \times 800$  mm sheets, is treated with

an 18-20 per cent sodium hydroxide solution (mercerization). In this operation the cellulose absorbs the sodium hydroxide solution and swells strongly. A large part of the residual hemicellulose is washed from it, intermolecular bonds are partially destroyed, and as a result a new chemical compound—alkali cellulose—is formed:



The reaction between the cellulose and the concentrated sodium hydroxide solution is a reversible one. The changes which occur in

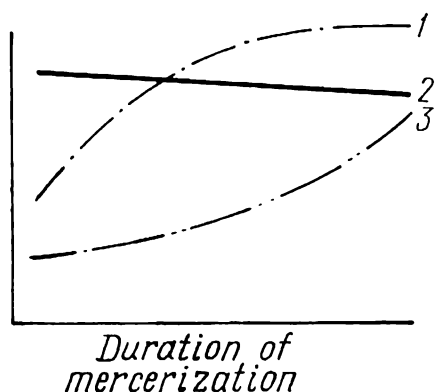


Fig. 103. The effect of the duration of mercerization on the properties of alkali cellulose:

1—amount of hemicellulose removed; 2—polymerization degree of the cellulose; 3—carboxyl-group content

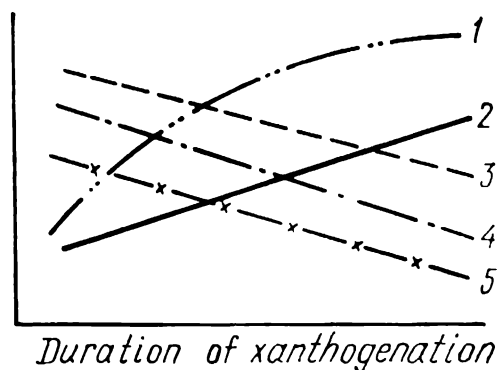


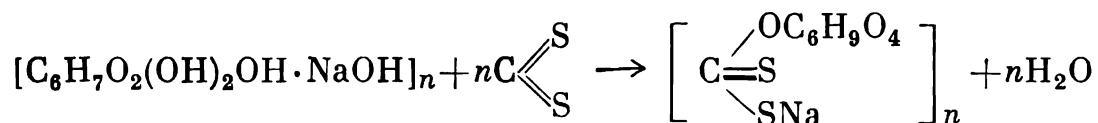
Fig. 104. The effect of the duration of xanthogenation on the composition and properties of the xanthogenate:

1—degree of esterification; 2—amount of thiocarbonates; 3—molecular weight of the regenerated cellulose; 4—viscosity of the viscose; 5—amount of free sodium hydroxide

the cellulose during the mercerization operation are shown in Fig. 103. Depending on the apparatus and the form in which the cellulose is used (sheets or a loose body) the process is carried out at a temperature from 20 °C to 50 °C and lasts from 10 to 60 minutes. The excess sodium hydroxide is pressed out of the alkali cellulose and directed to regeneration, where it is filtered, brought up to the necessary concentration, subjected to settling and is returned to the mercerization process.

The alkali cellulose is then disintegrated and aged under constant conditions (20-22 °C). During this operation of “preripening”, due to oxidation with the oxygen of the air in the alkali medium, the degree of polymerization of the cellulose is lowered; the viscosity of the spinning solution can be controlled within wide limits in this way. Following this, the destructured alkali cellulose is treated with carbon disulphide (xanthogenation of the cellulose). The reaction produces a yellowish-orange cellulose-xanthogenate, which, in contrast to the initial cellulose, is highly soluble in weak (4-7 per cent) sodium hydroxide solutions. The viscous solution produced is called

viscose. The xanthation reaction is described by:



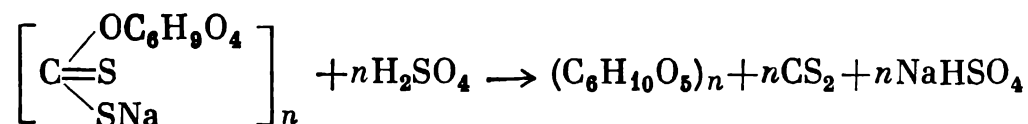
The composition and properties of the cellulose xanthogenate produced depend very strongly on the duration (Fig. 104) and temperature of the process and on the amount of carbon disulphide added.

All the operations are carried out either consecutively in four or five separate pieces of apparatus (bath-press, shredder, churn, solvent) or in a single viscose-manufacturing apparatus—up to and including final dissolution. The apparatus consists of a steel body with a water jacket for cooling. There are two Z-shaped churns which rotate at 900-1000 r.p.m. in the apparatus. They are designed for shredding the alkali cellulose and stir the mixture formed during preripening, xanthogenation and the first stage of dissolving.

Freshly prepared spinning solution cannot immediately be used for forming fibre. To produce so-called aged viscose the xanthate solution is purified to remove mechanical impurities from it in frame filter presses and is aged for some time (maturing of the viscose lasts from 24 to 60 hours) at a constant temperature (14-17 °C). In the aging process the chemical and colloid properties of the viscose change: its stability drops and its coagulation capacity increases. As a result of partial saponification of the xanthate, the degree of esterification of the cellulose is lowered. Air bubbles entrained by the solution slowly separate out, i.e. deaeration occurs. A representative viscose composition is: 6-9 per cent cellulose, 6-7.5 per cent sodium hydroxide, 2.2-2.3 per cent sulphur and 80-83 per cent water. After filtration and deaeration the yellowish ready for use xanthate solution is transferred by compressed air or a gear pump to the spinning section for formation into the fibre. A flow diagram of the spinning process is given in Fig. 105.

A small gear pump takes a fixed volume of the viscose and forces it through a filter. The viscose is then fed through a glass tube to a spinneret, immersed in a so-called coagulating tank, which contains an aqueous solution of sulphuric acid (80-150 g/l) and sulphate salts (160-320 g/l  $\text{Na}_2\text{SO}_4$  and 10-100 g/l  $\text{ZnSO}_4$ ) at a temperature of 45-50 °C. The spinning velocity lies between 75 and 100 m/min.

The following reactions take place in the tank: (1) coagulation of the viscose under the action of the electrolytes contained in the tank; (2) decomposition of the cellulose xanthogenate by the acid



and (3) decomposition of various sulphurous impurities contained in the viscose, with  $\text{H}_2\text{S}$  and  $\text{CS}_2$  being liberated.

Solution is continuously removed to the regeneration unit from which it is returned to the coagulation tank. The fibre, consisting of regenerated cellulose, is subjected to tension and is packed. Packing (Fig. 105) may be carried out either by a centrifugal or a bobbin method. In the first of them, the filament is caught up by a spinning disk and directed through a funnel to the bowl of a centrifuge fixed to an

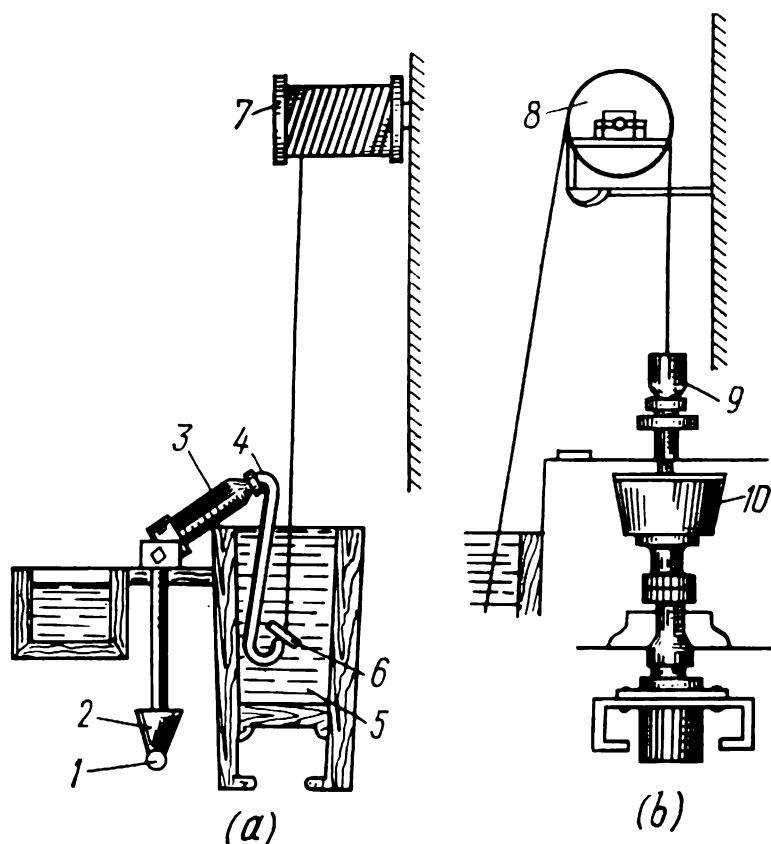


Fig. 105. Schematic diagram of the forming process:

(a)—bobbin spinning method; (b)—centrifugal spinning method; 1—viscose-solution pipe; 2—spinning pump; 3—filter; 4—glass tube; 5—bath; 6—spinneret; 7—bobbin; 8—spinning disc; 9—funnel; 10—centrifuge

electric spindle which revolves at 6000-10 000 r.p.m. In the coiling process, the yarn is also twisted to a certain extent (Fig. 105b).

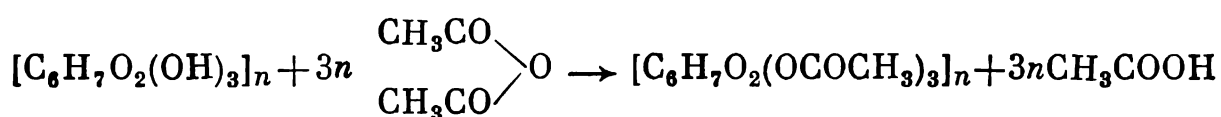
In the bobbin method (Fig. 105a) feeding of the spinning solution, formation and stretching of the filament all take place in the same fashion as above, but the thread from the stretching mechanism is coiled onto a rotating bobbin and it must later be twisted in a separate, special, twisting machine.

In the finishing plant the yarn produced is washed with softened water to remove acid, sulphates and soluble salts. Further finishing consists of the following operations: treating with a weak alkaline solution to remove sulphur (desulphuration), then with a weak acid solution to remove low-solubility salts, and bleaching to remove iron

and other coloured impurities. The fibre is then lubricated to give it the necessary softness and elasticity, and to make it slippery so that it will be easier to manufacture finished goods from the silk. After drying, the fibre is recoiled, graded, packed and shipped to the consumer.

The extensive use of viscose fibre is a result of the low cost and availability of the raw material. Viscose fibres withstand the action of organic solvents and are stable to temperatures of 100-120 °C for long periods. Their tensile strength varies from 20 (ordinary fibre) to 54 kg/mm<sup>2</sup> (high-strength fibre). Negative features of this fibre are low resistance to alkalis and considerable loss of strength when wet (up to 40-50%). Besides silk and staple fibre, cellophane, cord, bottle stoppers, artificial hair and Persian-lamb fur are also made from viscose.

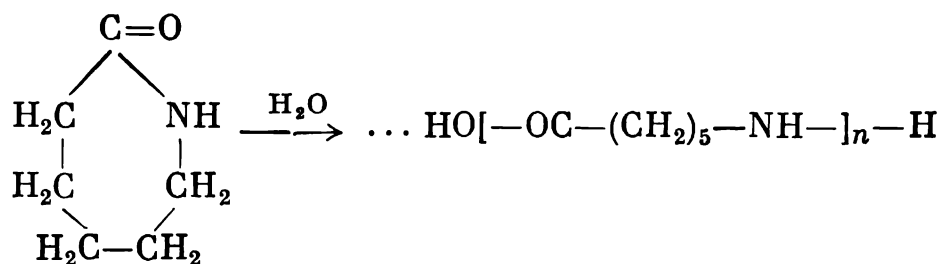
When cellulose reacts with acetic anhydride in the presence of acetic acid or methylene chloride and sulphuric acid or chloric acid as a catalyst cellulose acetate is formed, from which *acetate fibre* is made:



After being partially saponified, the cellulose acetate is dissolved in a mixture of acetone and alcohol (85 : 15) in vertical tanks with agitators. The spinning solution produced is subjected to filtration and deaeration and then sent to a unit for forming fibre by the dry method. The operation consists in pressing the hot spinning solution through spinnerets to form fine streams, which drop vertically down into the shaft of a spinning machine through a countercurrent of clean air heated to 55-70 °C, so that the solvent evaporates. The streams of the solution solidify and change into endless, thin, elastic fibres, which combine at the bottom of the shaft to form an untwisted yarn that is subjected to finishing operations.

The *polyamide fibre capron* is made from the resin capron, which is manufactured from the lactam of ε-aminocaproic acid, or caprolactam. The latter—a white powder—is produced from phenol, benzene or cyclohexane. Caprolactam is melted and dissolved. Distilled water in an amount equal to 5-10% of the weight of the lactam is added, it acts as an activator of the polymerization reaction. When dissolution is complete, approximately 1 per cent acetic acid, which is a stabilizer and regulates the molecular weight of the polymer, is added. The solution is then filtered and fed for polymerization to a steel autoclave. The polymerization operation is carried out in an atmosphere of pure nitrogen at 250 °C and 15 atm over a period of 10-11 hours.

At high temperatures the water opens the caprolactam ring and  $\epsilon$ -aminocaproic acid and then polycaprolactam (capron) are formed



During the polymerization process the liquid reaction mixture gradually thickens. The resin (high-molecular compound) end product is pressed out with nitrogen gas under pressure (3-4 atm) through the discharge hole into a trough with cold (10-12 °C) water. In the trough the polymer quickly solidifies into a hard, elastic, white ribbon (with a yellowish hue).

Caprolactam polymerization can be carried out as a continuous process. The ribbon produced is disintegrated in a chopping machine into flakes (7-8 mm). The unreacted monomer and other low-molecular compounds are then extracted with hot softened water (95-98 °C). The moisture is pressed out of the flakes, they are dried and melted at a temperature of 260-270 °C and fed in fixed portions at a pressure of approximately 60 atm through a filter to the spinneret by a metering pump.

The streams of melt flowing out of the spinneret enter into a high shaft in which they are cooled with air and solidify; the filaments formed are wound onto a bobbin. The yarn is stretched, twisted, washed, dried, rewound and oiled. The spinning rate in making capron and other synthetic fibres may be as high as 1500 m/min, i.e. much higher than for viscose fibres.

## 5. The Manufacture of Plastics

Plastics comprise an extremely wide group of synthetic materials, whose main components are naturally-occurring or synthetic high-molecular compounds, which are capable of changing, at high temperatures and pressures to a plastic condition, of being moulded by applied force and of solidifying and retaining the given shape during the life of the fabricated items.

**The high-molecular compound** is the principal component, which binds all the other components into a monolithic whole and gives the mixture (the composition) its plasticity, capacity to be moulded and also its electric insulating, anticorrosive, and other useful properties. Besides synthetic polymers, cellulose esters, protein substances, asphalts and tars are also used for obtaining these properties.

According to their composition plastics can be divided into the no-filler plastics, consisting of a pure polymer, or ones with only very

small amounts of admixtures, and filler plastics—mixtures containing fillers, plasticizers, dyes, stabilizing agents, solidifying agents and other admixtures uniformly distributed throughout the binder—the resin.

**Fillers** are solid substances which are introduced to give, or to improve, the necessary physical properties to the plastic: high strength, heat resistance, low shrinkage during solidification. The filler also reduces combustibility of wares made from the plastic and often increases water resistance, improves the appearance or dielectric properties. Both organic and inorganic compounds are used as fillers. They can be in the form of powders (wood-, mica- or quartz-meal, carbon-black, graphite, barium sulphate, kieselguhr, kaolin, talcum); fibres (cotton, asbestos, textile combings, glass fibre); and sheets (paper, cotton and glasscloth, mica, wood veneer). Table 18 contains a classification of plastics based on the filler in them.

TABLE 18

Classification of Plastics Based on the Fillers in Them

Class of filler	Filler	Plastic
No filler		Polyethylene, polypropylene, vinyplast, polystyrene, organic glass, fluoroplastic, polyvinylbutyral, polyamides, polyformaldehyde, polycarbonate, neoleukorite
Gas-air		Foam, porous, and honeycomb plastics: mipora, expanded polystyrene, foam phenoplast, polyurethane foam (porolon), etc.
Powder form	Wood meal, talcum, ground quartz, graphite, barite, aluminium oxide, etc.	Phenoplasts: monoliths, phenoliths, aminoplasts
Fibrous	Wood pulp, asbestos and glass fibre, textile combings, wood, glass, etc. crumbs	Fibre-filled phenol resin, press materials: asbestoresols, fibre-glass materials, faolites
Sheet form	Sheets of paper, cloth (coarse calico, chiffon), asbestos cloth, glass-fibre cloth, veneer	Hardened paper, cloth laminate, glass-fibre laminates, asbestos cloth laminates, wood laminates

**Plasticizers** are mainly low-volatility, liquid substances, which increase the plasticity of the composition at raised temperatures, and make the fabricated ware more cold-resistant, more elastic and resilient. When the content of the plasticizer is increased the tensile and compressive strengths of the polymer drop, but the impact strength



and stretching capacity increase sharply. The most commonly used plasticizers are castor oil, dibutylphthalate, tricresylphosphate and other comparatively available chemical compounds.

Dyes are used to give the composition the desired colour. **Hardeners**, for example hexamethylenetetramine (urotropine), cause some plastics (phenolformaldehyde, epoxy, unsaturated polyesters) to be converted to a solid state by forming polymers with a three-dimensional structure.

Other admixtures are also introduced into plastics, often in small amounts: accelerators, which give the necessary solidification rate at lower temperatures; stabilizers, which make the plastic capable of retaining its original properties for a long time; lubricants, which make pressing easier; foaming agents for making foam- and expanded plastics; luminescent agents, antiseptics, which protect the material against mold, etc.

Plastics are used as construction materials, in making diverse parts of all kinds of machines, apparatus, instruments and other technical devices, including those which must operate under highly corrosive conditions over long periods of time. The density of plastics varies from  $0.01 \text{ g/cm}^3$  (foam- and expanded plastics) to  $2.2 \text{ g/cm}^3$ . Most plastics are 4-6 times lighter than metals.

The excellent mechanical strength of plastics, which in some cases is as high as that of ferrous metals, is a very important property. Some plastics possess a very low friction factor, whereas others, on the contrary, are used as a high-friction material. A distinctive feature of plastics is their excellent dielectric properties and low heat conductivity, which is 100 to 500 times less than that of metals. Many plastics do not burn, some of them are highly conductive for light and radio waves. Important advantages of plastics are high resistance to the effects of the surrounding atmosphere and various corrosive mediums, their capability of being formed into ware of complex shape by the most efficient modern methods.

However, plastics also possess a number of negative features, the most important of which is lower resistance to heat, as compared to metals. Most plastics can be used at temperatures up to  $150^\circ\text{C}$ . Fig. 106 shows the temperature at which plastics begin to soften and deform. Moreover, some plastics "age"; this consists of oxidation, darkening, reduction of hardness and strength.

USSR standards divide the hundreds of kinds of plastics manufactured in the country into four classes, depending on the chemical composition of the resin.

1. Plastics which contain high-molecular compounds produced by chain polymerization. This class includes plastics based on polymers of ethylene and its various derivatives, polymers of vinyl alcohol and their derivatives, polymers of esters of ethylene carboxylic acids, etc.

2. Plastics based on high-molecular compounds produced by polycondensation and by stepwise polymerization: phenolaldehyde resins (phenolic plastics), amido and amino formaldehyde resins (aminoplasts), organosilicon polymers, polyesters, etc.

3. Plastics based on modified naturally occurring polymers: ethers and esters of cellulose (celluloid, cello, Etrol), protein substances (for example, galalith), etc.

4. Plastics based on naturally occurring and petroleum asphalts.

Plastics of a mixed nature can also be produced, i.e. plastics containing resins of different classes, and this makes it possible to manufacture materials of even more diverse properties.

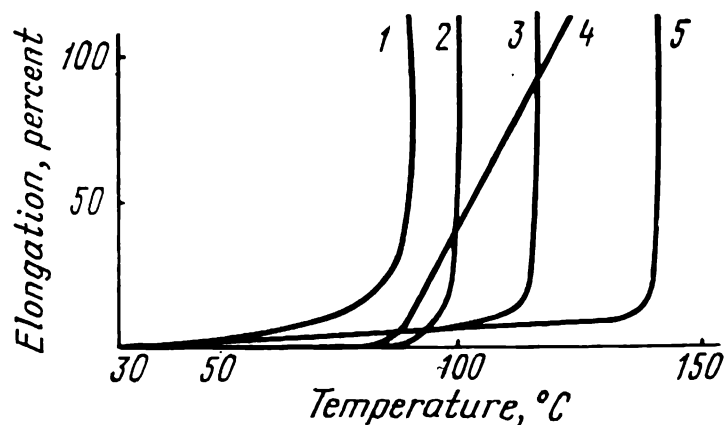


Fig. 106. The change in the strength of various high-molecular compounds with temperature:

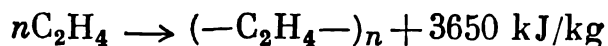
1—high-pressure polyethylene; 2—polymethylmetacrylate; 3—low-pressure polyethylene; 4—polyvinylchloride; 5—polypropylene

The most commonly used of the **polymerization resins** are: polyethylene, polystyrene, polymers and copolymers of vinyl chloride, polymers of fluoroderivatives of ethylene, polyacrylates, polypropylene, polyvinylacetate, polyisobutylene, polyformaldehyde and some others. Plastics based on these resins are thermoplastic and they are made without fillers; they possess excellent dielectric properties, high impact strength (with the exception of polystyrene), but most of them have low resistance to high temperatures.

The manufacture and properties of polyethylene ( $-\text{CH}_2-\text{CH}_2-$ )<sub>n</sub> can be considered as an example. It is made from ethylene in three different ways: (1) polymerization at a pressure of 1000 to 2000 atm and temperature of 180-220 °C with a small amount of oxygen (0.05-0.1 per cent) used as an initiator; (2) polymerization at atmospheric pressure or at a relatively low pressure (2-6 atm) and relatively low temperature (60-80 °C) with organometallic complex catalysts in a liquid-hydrocarbon medium, with no moisture or oxygen present; (3) polymerization at a pressure of 25-70 atm and a temperature of 130-240 °C over an oxide catalyst (Cr<sub>2</sub>O<sub>3</sub>, CrO<sub>3</sub>, etc.).

Polyethylene made by the last two methods (low-pressure polyethylene) has a strictly linear structure, a higher molecular weight (up to

70 000) and a melting point at least 20° above that of high-pressure polyethylene, whose structure is somewhat branched. The change in the principal mechanical properties of polyethylene with the molecular weight is shown in Fig. 107. Polymerization of ethylene at a high pressure is a chain reaction with a radical mechanism in which large amounts of heat are liberated:



Because of this, continuous removal of heat and a strictly controlled temperature are necessary for a normal course of the process. The rate of polymerization and the yield of the polymer depend on

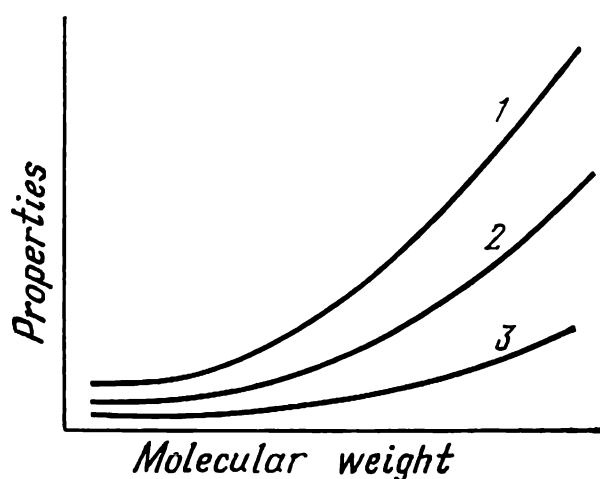


Fig. 107. The mechanical properties of polyethylene as a function of its molecular weight:

1—tensile strength; 2—elongation; 3—tensile strength at low temperatures

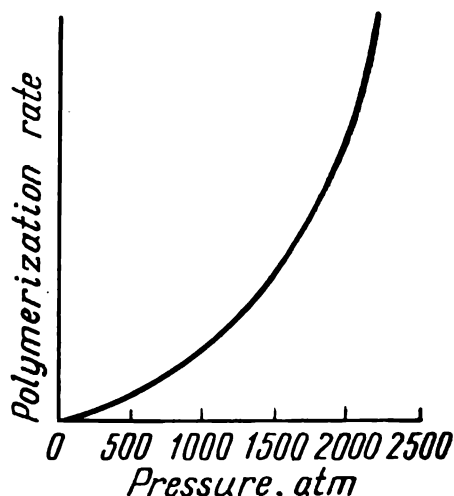


Fig. 108. The effect of pressure on the rate of ethylene polymerization

the purity of the initial gas (the ethylene content is not less than 99.9-99.99%), the amount of initiator used, the temperature and the pressure. Thus, raising the pressure results in an increase in the polymer yield and a higher process rate (see Fig. 108).

Polymerization of ethylene under pressure (Fig. 109) is carried out either in a tubular unit or in a reactor with an agitator. Ethylene containing the necessary amount of oxygen flows from the gas holder to a compressor, where it is brought up to a pressure of 1200-2000 atm, and then through an oil separator. Bulk polymerization occurs in the reactor at a temperature of 200-250 °C. The reactor, which operates roughly in plug flow conditions, consists of a system of thick-walled, inclined tubes with an inner diameter of 25 mm, formed into a long coil (300-400 m). The mixture of molten polyethylene and unreacted ethylene produced passes through a gas separator (where the pressure is 250-300 atm) and then to a separator-tank (pressure is 1-3 atm). When the pressure is reduced the occluded gas

is separated from the polymer and the latter is transferred to stabilization, dyeing and prilling units. Ethylene from the trap is transferred to a scrubber. Conversion of ethylene into the polymer during one pass through the reactor varies from 10 to 20 per cent. The overall degree of ethylene conversion achieved by recycling approaches 95-97 per cent. Tubular reactors are very cumbersome and other types

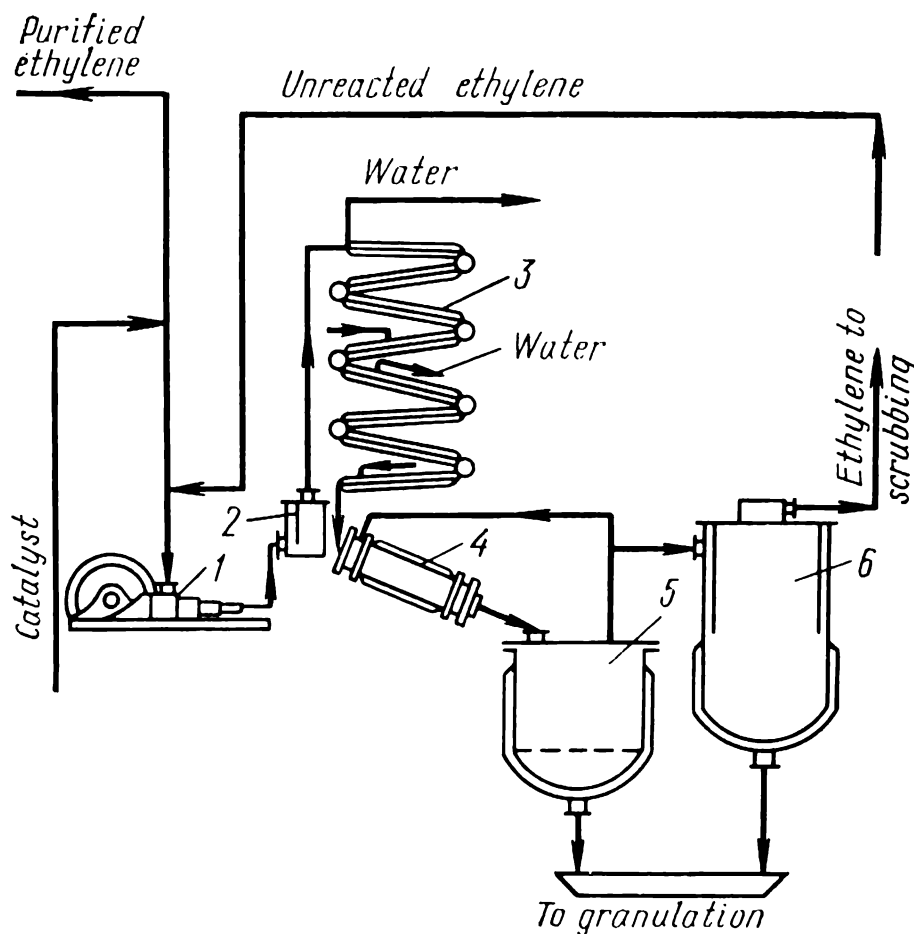


Fig. 109. Flow diagram of high-pressure polyethylene-manufacturing process: 1—compressor; 2—oil separator; 3—tubular reactor; 4—gas separator; 5—settling tank; 6—trap

of reactors are therefore used for carrying out polymerization. The reactor with a high-speed agitator for polymerization of ethylene at high pressures (Fig. 110) is a thick-walled (125-150 mm) vessel 5 to 6 m long. Conversion of ethylene to polyethylene is more complete in such a reactor; however, if the agitator stops this results in complete disruption of the process and, possibly, even an explosion.

Articles made of high-pressure polyethylene cannot be used at temperatures over 80 °C at which deformation will occur. The polyethylene has excellent dielectric properties, elasticity (it bends without breaking even at -60 °C), and high stability to diverse corrosive mediums. It is used for making films, sheets, tubes, blocks, insulation, hoses, and diverse formed- and cast items. The polyethylene can be subjected to all types of mechanical treatment, it can be glued and welded.

From year to year ion polymerization of ethylene in the presence of the heterogeneous Ziegler complex catalyst is being used more and more extensively. The catalyst is a complex compound of tetrachlorated titanium and triethylaluminium (or another co-catalyst).

In this method purified ethylene is introduced into a suspension of the organometallic complex catalyst in low-boiling benzene (the

reaction temperature is 60-80°C); the unreacted ethylene is separated from the polymer and the catalyst in a system of separators and, after it is purified, it is returned to the process; the polymer separated is subjected to further treatment. The process can be carried out either batchwise or continuously. Approximately 1.1 t of ethylene, 2.4 kg of triethylaluminium and up to 4.8 kg of tetrachlorated titanium are consumed per ton of commercial polyethylene produced.

Intensive scrubbing and purification of the polymer produced to remove remnants of the catalyst, and oxides of titanium and aluminium formed by its decomposition, are very important. Their presence in the polyethylene sharply lowers the quality of the product.

The polycondensation group includes phenol-aldehyde, amino-formaldehyde, polyester, epoxy, polyamide, and silicone resins. Some of them are thermoplastics,

but most are of the thermosetting type. Ware made from plastics based on these resins can be used for long periods of time in a wider temperature range; at high temperatures the changes in their physical and mechanical properties are not so pronounced as in the case of articles made of most of the polymerization resins. However, these resins are more friable.

**Phenol-aldehyde resins** are produced by polycondensation of phenols or analogous compounds—cresol, xyleneol—with aldehydes (formaldehyde, acetaldehyde, furfural, etc.) in the presence of catalysts (acid or alkaline). Intermediate products are formed in the reaction which are capable of reacting further to form more complex

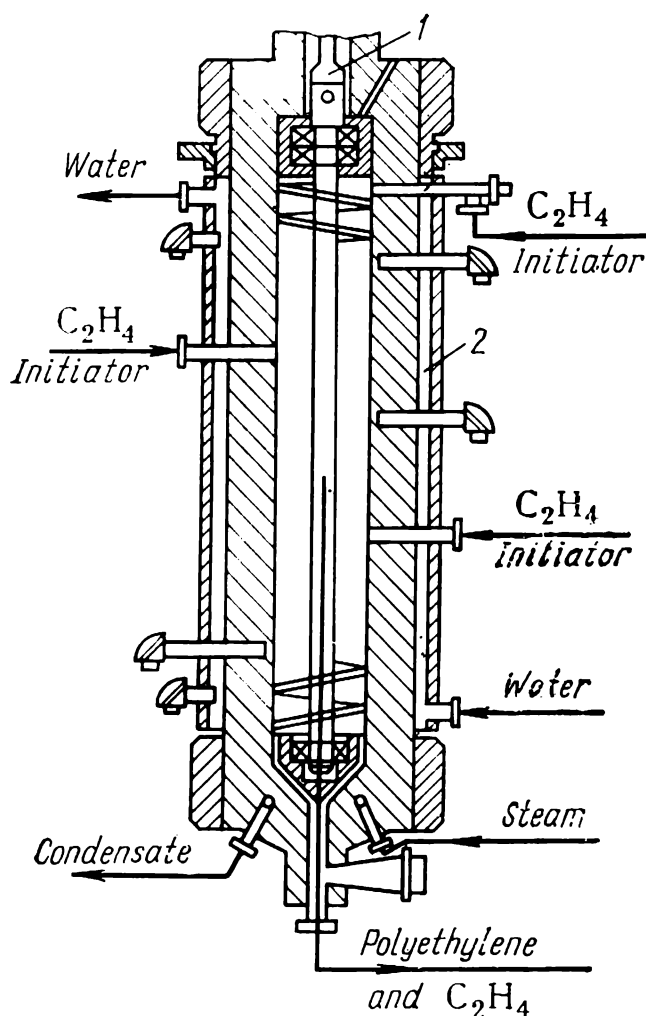


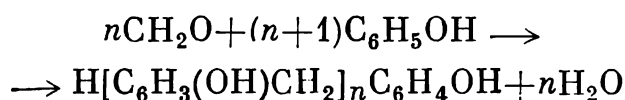
Fig. 110. A stirred reactor for high-pressure polymerization of ethylene:

1—agitator; 2—jacket

condensation products. This diversity results from the presence in the phenol nucleus of three mobile hydrogen atoms capable of taking part in substitution reactions.

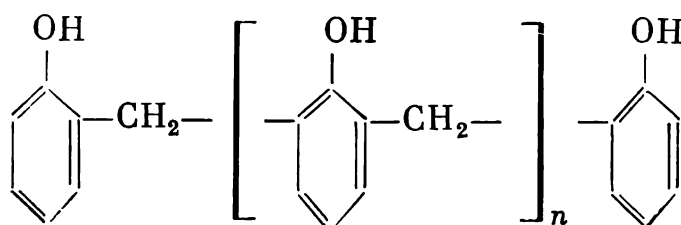
Polycondensation of phenol with aldehydes produces resins of two types—thermoplastic and thermosetting resins.

**Thermoplastic resins** known as novalaks are obtained when there is an excess of phenol in the initial mixture (7 moles of phenol per 6 moles of formaldehyde) and if acid catalysts (for example, hydrochloric acid) are used. The reaction leading to formation of novolak resins can be written as follows:



where  $n = 4-8$ . The equilibrium constant of the reaction is very large ( $K = 10\,000$ ), i.e. practically, the reaction is shifted to formation of the resin. The water liberated in the process has only an extremely small effect on the equilibrium and the rate of the process, and the basic factors which determine the direction of the reaction and its kinetics are the temperature, the duration of the reaction, and the nature and concentration of the catalyst employed. As is evident from Fig. 111 the process rate grows with an increase in the content of the catalyst or the formaldehyde in the initial mixture. It follows, that production of phenol-formaldehyde resins is a homogeneous, catalytic process (the initial materials and the catalyst are in the liquid phase) which forms, however, a heterogeneous L-L system of two immiscible liquids.

The structural formula of the resin which has a linear structure is



The lower the molar ratio of phenol to formaldehyde, the higher will the molecular weight of the resin obtained be. Increased duration of polycondensation results in more complete combining of phenol with formaldehyde and in growth of the mean molecular weight

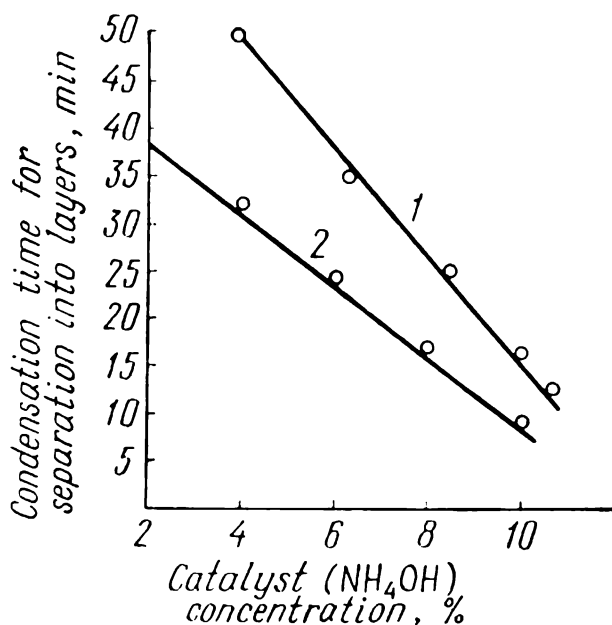
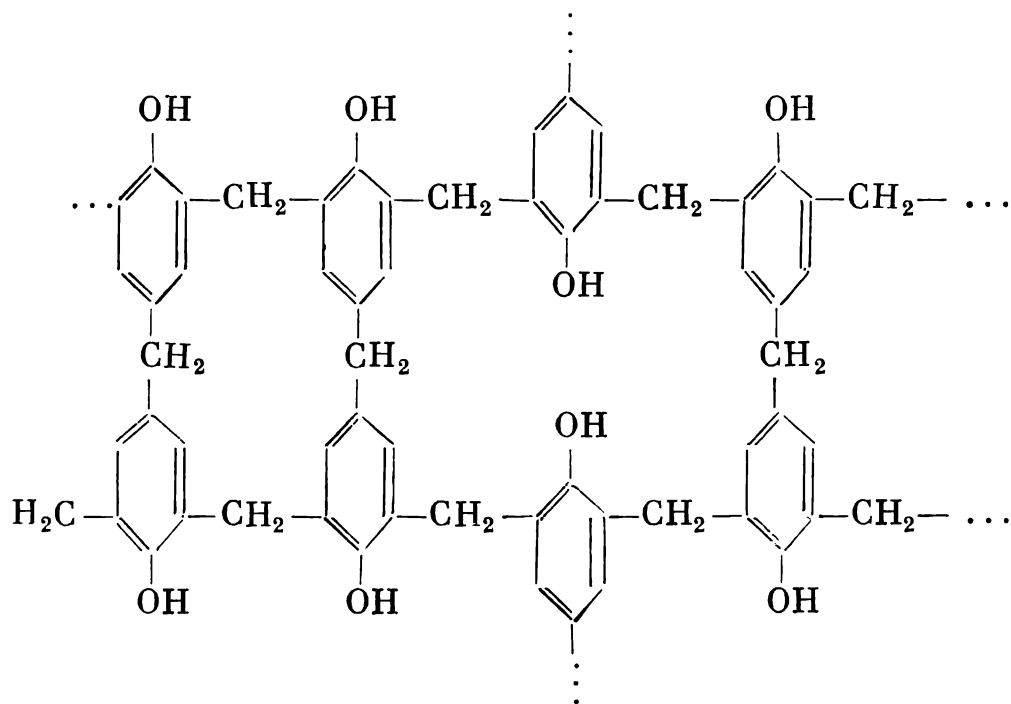


Fig. 111. Rate of condensation of formaldehyde and phenol vs catalyst concentration:

1—35.6% formaldehyde; 2—33.2% formaldehyde

of the end product. To convert a novolak resin into a non-melting and insoluble solid, it must be subjected to additional processing—heating with paraformaldehyde or hexamethylenetetramine (urotropine).

**Thermosetting phenol-formaldehyde resins**, known as resol resins, are produced if the formaldehyde is taken in excess (7 or more moles formaldehyde per 6 moles phenol), usually in the presence of an alkaline catalyst. When resol resins are heated they form a body which does not melt and is insoluble. Depending on the degree of hardening, three states of the resol resins are distinguished: (a) *resol* (or bakelite A)—a mixture of high-molecular products which melts when heated, is soluble in alcohol or acetone and has a linear structure; (b) *resitol*—the second stage (or bakelite B); resol is transformed to this form when it is heated, or during lengthy storage. Resitol, which has a branched structure, is only partially soluble in alcohol or acetone but swell strongly in them; when heated it does not melt, but softens and becomes elastic; (c) *resite* (or bakelite C) is the product of the last stage of polycondensation (at higher temperatures and pressures); it does not melt and is insoluble. Resite does not even soften when heated and it does not swell in solvents. The hardening results from the binding together of the long linear chains with cross-links:



The molecular weight of resol resins lies between 400 and 1000.

Novolak and resol resins are manufactured commercially both as dry and liquid products and also in the form of emulsions and varnishes. The manufacturing process consists of the following basic operations: (1) preliminary treatment of the raw materials (melting the phenol, preparing the formalin); (2) metering and feeding the raw materials to the reactor; (3) condensation (cooking) of the resin;

(4) drying the resin and removing it from the reactor; (5) cooling the resin end product and final processing.

Phenol-formaldehyde resins are produced both by batch-type and continuous-action processes. In the batch process the reactor is an alloy steel, nickel or bimetal cylindrical vessel with a capacity of 5-15 m<sup>3</sup>. The spherical bottom is furnished with an outlet pipe containing a valve through which the resin end product is discharged.

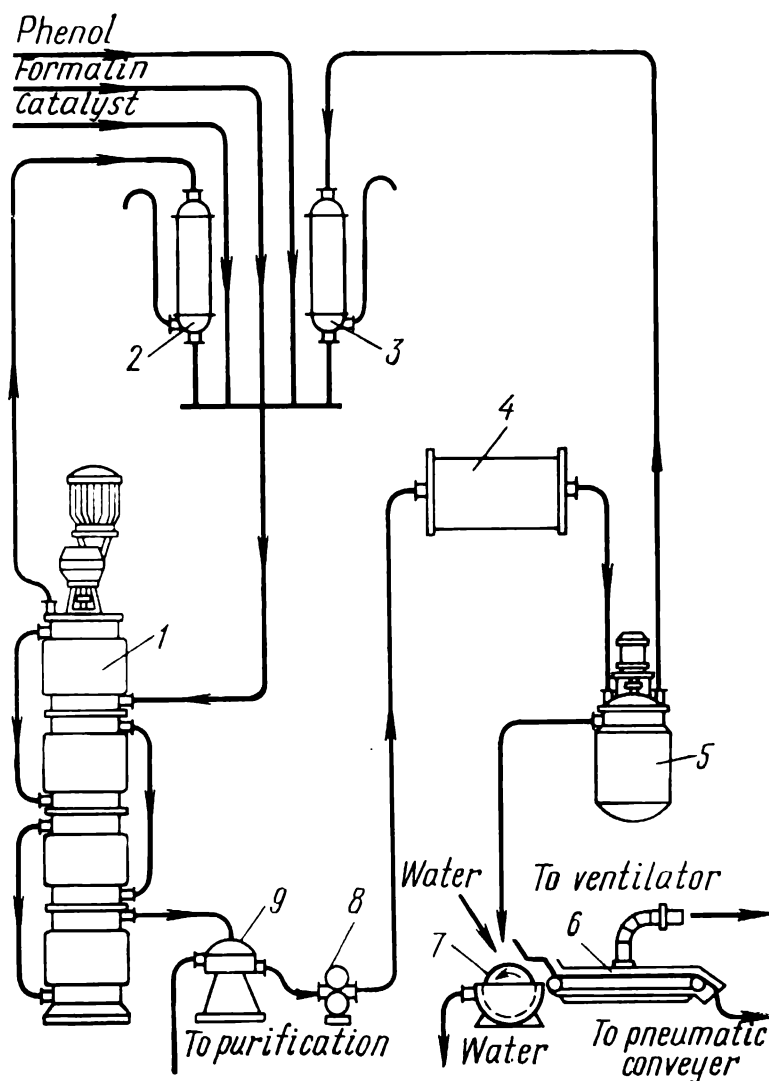


Fig. 112. Flow diagram of continuous-process manufacture of novolak phenol-formaldehyde resins:

1—completely mixed reactor; 2, 3—coolers; 4—dryer; 5—resin reservoir; 6—belt conveyer; 7—drum cooler; 8—pump; 9—separator

The cover contains a charging opening and has windows in it. The reactor, which operates at roughly complete mixing, is supplied with an anchor-type agitator and a water jacket for heating (cooling) the reaction mixture.

Reactors made up of a number of complete-mixing sections are employed to achieve continuous polycondensation (Fig. 112). The apparatus is in the form of a tower with the sections located one above the other (Fig. 113). The agitators in all the sections are at-



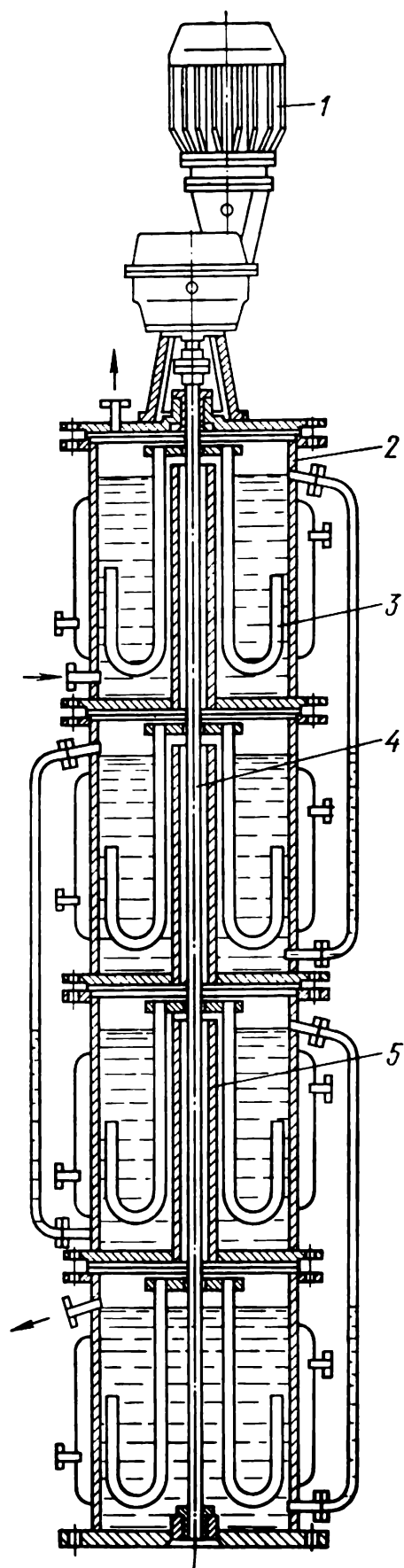


Fig. 113. Continuous-polycondensation reactor:

1—electric motor and reduction gear; 2—tower section; 3—agitator; 4—common shaft; 5—sleeve

tached to a common shaft and are rotated by a single electric motor. All the initial materials are introduced into the "mixed" tower at atmospheric pressure and a temperature of 95-98 °C. The resin formed is removed from the water in a separator and is transferred to a drier, to a resin reservoir and is then cooled.

Phenol-formaldehyde resins are used in diverse ways: (a) without a filler—cast resites; (b) as moulding compositions (with a powdered or a fibrous filler); (c) as a binder for laminated plastics; (d) as an adhesive, or as a varnish for covering metals or wood; and (e) for making cellular plastics.

The most important are the moulding compositions. They are made both by dry (rolling- or worm-screw) and wet process techniques. In the latter case an aqueous emulsion of the resin is first carefully mixed with the other ingredients and the mixture is then dried, or the ingredients are impregnated with a solution of the resol resin in alcohol. The most commonly used is the roller process, which is accomplished with simpler equipment. The process can also be carried out in worm-screw type machines, where mixing, impregnation of the filler with the molten resin and plasticization of the mixture all take place.

If a long-fibre material is impregnated with the resin and then moulded a material of high strength is produced. To lower the friability of a resite, the resol resins are melted together with a thermoplastic resin or with rubber.

Moulding is based on the plasticity of materials at high temperatures. The plasticity of thermosetting materials is gradually reduced when they are heated. The basic factors governing a moulding process are the temperature, duration of the process, and pressure used. Plastic ware is made in plastics processing in industry by pressing, casting under pressure, extrusion, stamping, or by gluing and welding separate parts or sheets and by some other operations. The selection of the method to use in making a given article depends on the nature of the material and its type (thermosetting or thermoplastic), the shape of the article, etc. After pressing, casting or moulding, the articles are machined to remove burrs and casting runners.

## 6. The Manufacture of Rubber and Synthetic Rubber

Elastic high-molecular compounds which can be greatly deformed by an external force and recover rapidly when the load is removed are known as rubbers. The elastic properties are retained over a comparatively wide temperature range. Rubbers are divided into natural and synthetic ones.

For many years rubber was made exclusively from the latex (sap) of the tropical tree *Hevea*.

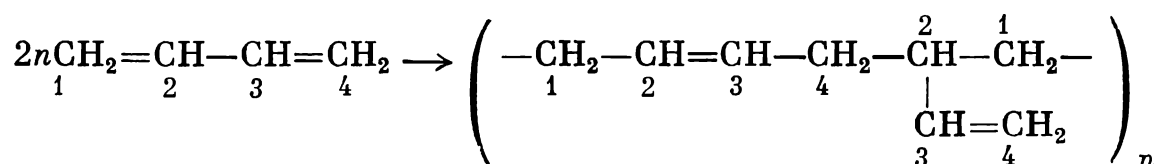
Due to the continuously growing demand for rubber scientists all over the world many years ago began to seek ways of making it synthetically. For a long time the efforts made along these lines by scientists, which already began before the First World War, were unsuccessful. Only in 1928 did the Soviet scientists S. V. Lebedev and B. V. Byzov solve this important problem independently of each other. In the USSR the Lebedev process for making synthetic rubber was applied commercially. By this method the initial material—*butadiene-1,3* (divinyl)—is produced from ethyl alcohol using a mixture of catalysts developed by Lebedev. This is followed by polymerization of the butadiene in the presence of metal sodium to produce the rubber.

The assortment of synthetic rubbers is continuously growing. In 1945 only 6 types of rubber were manufactured, but now several tens of kinds are made. They can be divided, according to the initial raw material used, into two classes: rubbers made from a single monomer, and copolymer rubber (made from two or three monomers). Depending on the applications of the synthetic rubbers they can arbitrarily be divided into two groups: general-purpose rubbers, used for making tyres and most other rubber goods, and special purpose rubbers. The latter possess properties which allow them to be employed in rubber goods for use under hard conditions, where a certain property of the rubber is of special importance: stability to high temperatures (up to  $+250^{\circ}\text{C}$  and even higher); frost-resistance (down to  $-60^{\circ}\text{C}$  and lower); electrical conductivity; chemical sta-

bility to acids, alkalies, oxidizing agents, organic solvents, liquid fuels, lubricants, gases, etc. (see Table 19). In recent years production of butadiene synthetic rubber has decreased continuously and production of stereoregular (polybutadiene, or divinyl, and polyisoprene) rubbers, whose properties are better than those of natural rubber in a number of ways, has grown.

Wares made of rubber and vulcanized rubber have become indispensable in all branches of the economy and in making consumer goods. This is due to its unique properties. The high strength and elasticity are utilized to soften shocks and dampen vibrations and together with good wearing properties this makes them an ideal material for making tyres, inner tubes and rubber shoes. Their resistance to the chemical effects of many substances and their high resilience have led to their use in making diverse sealing devices. Such properties of rubber as softness and retention of rupture strength under repeated bending have resulted in its utilization for manufacturing transmission and conveyer belts. Moreover, rubber is gas- and water-impenetrable and a good dielectric, and this is utilized in the electrical industry, and has also led to its being employed in making all sorts of covers, balloons, dirigibles, inflated boats, space suits, etc.

Polymerization of pure butadiene is carried out by two modifications of the mass process: (1) bulk polymerization (see p. 245) in the liquid phase (liquid-phase rubber) and (2) in the gas phase (gas-phase rubber). Both processes are carried out batchwise in steel autoclaves with a capacity of 2.7 m<sup>3</sup> and designed to operate at a pressure of 9-10 atm and a temperature of 30-40 °C. Metal sodium is used as the catalyst and the product is called sodium-butadiene rubber. In bulk polymerization a polymer (molecular weight from 80 000 to 200 000) is formed by the joining of butadiene molecules at the 1,2 and 3,4 sites:



The highly-branched structure of sodium-butadiene rubber, i.e. the presence of a very large number of side vinyl groups, has a negative effect on its elastic and other properties.

The polymerization rate and the properties of the rubber depend on uniform distribution of sodium in the butadiene, on the interphase contact area between them, the purity of the monomer, the pressure and the temperature. Strict control of the temperature is necessary, since after primary active centres are formed polymerization proceeds with liberation of heat. After polymerization has ended, the unreacted monomer and other residual components are evaporated from the autoclave. Nitrogen is then fed to the autoclave, and the rubber is discharged.

TABLE 19

The Most Important Kinds of Synthetic Rubber

Type of rubber	Initial monomers	Specific properties
<i>General-Purpose Rubbers</i>		
Sodium-butadiene	Butadiene $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$	
Divinyl-styrene	Butadiene and styrene $\text{CH}_2=\text{CH}$   $\text{C}_6\text{H}_5$	
Divinyl-methyl-styrene	Butadiene and methylstyrene $\text{CH}_2=\text{C}-\text{C}_6\text{H}_5$   $\text{CH}_3$	
Isoprene	Isoprene $\text{CH}_2=\text{C}-\text{CH}=\text{CH}_2$   $\text{CH}_3$	
<i>Special-Purpose Rubbers</i>		
Butadiene-nitrile	Butadiene and acrylonitrile $\text{CH}_2=\text{CH}-\text{CN}_2$	High resistance to heat, petrol and oil
Chloroprene (neoprene)	Chloroprene $\text{CH}_2=\text{C}-\text{CH}=\text{CH}_2$   $\text{Cl}$	High resistance to heat, petrol, ozone and oil. Can be used as a general-purpose rubber
Polyisobutylene	Isobutylene $\text{CH}_2=\text{C}$   $\text{CH}_3$   $\text{CH}_3$	Chemical stability
Butyl rubber	Isoprene and isobutylene	Gas-proof and chemically stable
Thiokol	Dichloroethane, $\text{ClCH}_2-\text{CH}_2\text{Cl}$ , or dichloroethylether $\text{ClCH}_2-\text{CH}_2-\text{OCH}_2-\text{CH}_2\text{Cl}$ , and sodium tetrasulphide, $\text{Na}_2\text{S}_4$	Resistance to oil and petrol
Urethane polyester	Diisocyanate, $\text{O}=\text{C}=\text{N}-(\text{CH}_2)_n-\text{N}=\text{C}=\text{O}$ , and a dihydric alcohol, $\text{HO}-(\text{CH}_2)_n-\text{OH}$	High strength and resistance to wear
Silicone	Organosilicon compounds $\text{R}$   $\text{HO}-\text{Si}-\text{OH}$   $\text{R}$	Can be used in a wide temperature range, from $-60^\circ$ to $250-300^\circ \text{C}$

The emulsion polymerization process (see p. 245) is a continuous, high-capacity process, which provides a large output of synthetic rubber with uniform properties. The process can easily be controlled, local overheating is avoided, copolymerization of two or more monomers is possible and due to these advantages the method is predominant.

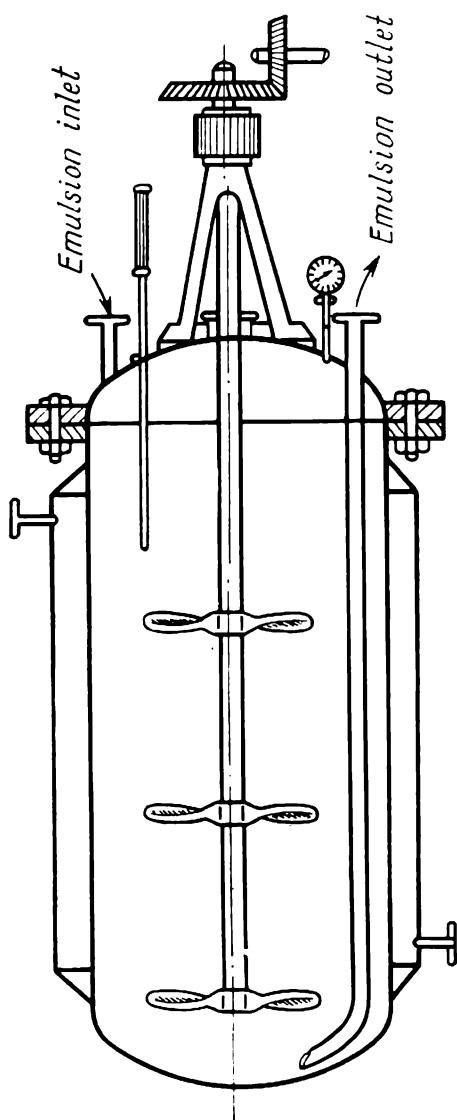


Fig. 114. Emulsion-polymerization reactor

Most extensively employed for making tyres and other rubber ware at present are isoprene and butadiene-styrene rubbers. Copolymerization is carried out in an aqueous medium at a temperature of from 5 to 50 °C in a battery of consecutive interconnected polymerization units. Water and an emulgator (for example, rosin soap) are added to a preliminarily composed mixture of butadiene with styrene in a pre-emulgation apparatus. The emulsion is continuously pumped into the first polymerization unit together with a solution of an initiator and a regulator. Eleven of the twelve reactors in the battery are always in operation. The polymerization vessels are made of a bimetal or lined with an acid-resistant enamel; they have an individual capacity of 12-20 m<sup>3</sup>, and are furnished with an agitator with three horizontal blades (Fig. 114). The agitator can revolve at

from 50 to 1450 r.p.m. The polymerization unit has a water jacket to which either hot water (during the starting-up period), or cold water (to remove heat liberated in the reaction) is fed. The process is carried out with continuous stirring and with the mixture, containing admixtures of the regulator, flowing through the entire battery of polymerization vessels at such a rate as to provide polymerization of 58-60 per cent of the original hydrocarbon mixture during the residence-period.

The unpolymerized monomers are removed from the latex produced, after which the latex is transferred to further processing. Electrolytes (NaCl or CaCl<sub>2</sub> and H<sub>2</sub>SO<sub>4</sub> or CH<sub>3</sub>COOH) are added to precipitate the rubber from the latex. The coagulated rubber is trans-

ferred to a steel sieve (Fig. 115), where it is washed, dehydrated and formed into a rubber ribbon, which is dried with hot air and powdered with talcum, and then coiled into rolls.

The sorts of butadiene-styrene rubbers differ both in the conditions of polymerization and in the ratio of monomers in the initial hydrocarbon mixture. Thus, polymerization at low temperatures (5 °C or even below zero) produces a "cold" or "low-temperature" rubber, which has a higher molecular weight and gives a vulcanized rubber of higher strength and better resistance to wear. The most commonly

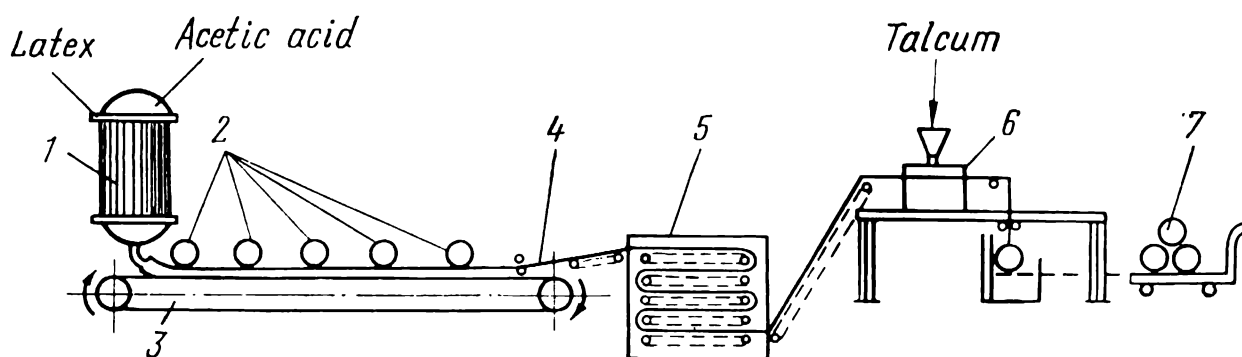


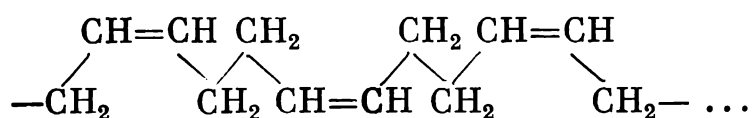
Fig. 115. Making rubber from latex on a ribbon-casting machine:

1—coagulator; 2—spreader rolls; 3—endless sieve belt; 4—rubber ribbon; 5—dryer; 6—powdering with talcum; 7—coiled rubber

used ratio is 70 parts by weight of butadiene to 30 parts by weight of styrene. A further increase in the styrene content reduces the elasticity of the rubber.

Other types of butadiene-styrene rubber are also produced: with an oil filler, carbon-black filler, and containing admixtures of both oil and carbon black—"carbon-black oil" rubber. To make such a rubber 10 to 30 per cent mineral oil is added to the synthetic latex so as to form an emulsion. Rubber wares made of oil-filler rubber are soft and pliable. Mixing the latex with highly dispersed carbon black or with a carbon black plus an oil emulsion prior to coagulation produces a rubber with high resistance to wear.

In polymerization in solutions using special stereospecific catalysts (lithium, lithium alkyl) or complex-compound organometallic catalysts rubbers with a stereo-regular structure, known as *cis*-1,4-polybutadiene rubbers, in which the molecular links are joined at the 1,4 sites ("head to tail"), are formed:



*Cis*-1,4-polyisoprene is made in the same fashion. The strictly regular structure of the chains of these rubbers gives them excellent mechanical properties. Especially with respect to its dynamic and elastic properties, unfilled synthetic isoprene rubber is not inferior to natu-

ral rubber and it is just as easy to process; its tensile strength lies between 270 and 300 kg/cm<sup>2</sup>.

*The manufacture of rubber articles* consists of three principal stages: preparing the rubber composition, forming the article, and vulcanizing. Rubber compounding consists of the following operations: (1) preparing the gum and the other ingredients (weighing and metering, impregnating cloth with the gum, cutting it, etc.); (2) preparing the rubber composition (mixing); and (3) forming the mixture into sheets. Various organic and mineral ingredients are added to the gum. The mixture must be properly composed to obtain high-quality articles with the required properties. The principal component on which the property of the ware mainly depends is the rubber. Besides, the following materials are added to the composition: vulcanizing substances—sulphur and organic peroxides; vulcanization accelerators—diphenylguanidine, dithio-*bis*-benzothiazole, tetramethylthiuramdisulphide (thiuram), mercaptobenzothiazole; softeners—dibutylphthalate, fatty acids, vaseline, pine tar, Ruberax (an asphalt), paraffin; antiagers—phenols, wax, phenyl- $\beta$ -naphthylamine; active fillers—carbon black, silica, white zinc, kaolin; pigments. An increase in the strength of the bonds between the rubber and the particles of the active filler results in increased strength of the rubber articles. The ingredients added to the composition improve the technological properties of the rubber mixture and the quality of the fabricated ware. By vulcanization at high temperatures (130-160 °C) and pressures (3-6 atm) sulphur is chemically joined to the linear rubber molecules and cross-links them into a three-dimensional rubber structure.

### 1. Environmental Protection and the Necessity of Cleaning Industrial-Wastes Discharges

The problem of protecting the environment from pollution and contamination by various types of discharges is now in the focus of attention all over the world. Together with the development of industry and transportation, and also with the growth in the assortment of chemicals, there is a continuous increase in pollution of the biosphere\* by industrial and other effluents. This is a global process which has two principal aspects—pollution of the atmosphere and pollution of the aquasphere. The problem created by the continuous, accelerated pollution of the atmosphere, especially in the environment of large cities and industrial centres is extremely acute. At present hundreds of millions of tons of diverse substances which are a source of harm to the health of people, plant life, and useful microorganisms are discharged to the atmosphere. The volume of these discharges to the atmosphere is continuously increasing together with industrial growth; in the last decade the volume has doubled and in a number of large industrial cities and centres the concentration of harmful impurities is already impermissibly high and the level is dangerous for health and plant life.

The principal sources of harmful effluents to the atmosphere are heat-power plants, automobiles and industrial plants. Automobiles now discharge approximately 200 million tons of carbon monoxide and 50 million tons of diverse hydrocarbons to the atmosphere. The major contribution is made by heat-power plants whose stack gases carry hundreds of millions of tons of ash and sulphur dioxide into the air per annum. Industrial plants discharge a great diversity of contaminants to the air in the form of aerosols, gases and vapours.

We shall consider, as an example, contamination of the atmosphere with sulphur dioxide. At the second international congress on combatting pollution of the atmosphere in December, 1970, it was noted that 146 million tons of sulphur dioxide was discharged to the atmosphere in 1964. This was two and a half times more than the total consumption of sulphur dioxide in manufacturing sulphuric

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\* The biosphere is the outer envelope of our planet, which borders with the atmosphere, aquasphere and lithosphere—the habitat of living matter, i.e. the aggregate of the organisms which populate the earth.



acid. The major source of  $\text{SO}_2$ -contamination are heat-power plants which burn solid and liquid fuels, ferrous- and non-ferrous metallurgy and sulphuric acid plants. The sulphur content of solid fuels (peat, shale, coal) varies between 0.5 and 2.5%, and that of liquid fuel (heating oil)—between 1.0 and 7.0%. When the fuel burns the sulphur is oxidized to the dioxide whose concentration in the stack gases is from 0.1 to 0.5%.

The non-ferrous metals—copper, zinc, nickel and others—are produced mainly by burning sulphurous ores. At many plants the metallurgical processes are carried out so as to obtain a gas which can be utilized to make sulphuric acid. However, some of the effluents containing from 0.2 to 3.0%  $\text{SO}_2$  are directly discharged to the atmosphere. In non-ferrous metallurgy the principal sources of  $\text{SO}_2$  are coking batteries and agglomeration plants, whose stack gases contain up to 3% sulphur dioxide. In manufacturing sulphuric acid discharge of  $\text{SO}_2$  to the atmosphere is a result of incomplete oxidation in catalytic converters and in nitrous acid towers; the  $\text{SO}_2$  concentration of the stack gases lies between 0.1 and 0.3%. An important source of  $\text{SO}_2$  pollution of the atmosphere and the aquasphere is the pulp-and-paper industry. All the sulphur dioxide employed in making pulp by the sulphite process is transferred to the aqueous and gaseous discharges of the manufacturing plants. Part of the discharge of  $\text{SO}_2$  to the atmosphere is due to other chemical processing plants—the manufacture of synthetic fibres, explosives, pigments, etc.

Contamination of the atmosphere is accompanied by very dangerous to humanity pollution and contamination of the aquasphere by aqueous discharges of industry, agriculture, public services, petroleum tankers, etc. As a result in many countries there is an acute deficiency of fresh water and drinking water, especially in industrial and agricultural regions.

Industrial plants discharge huge volumes of aqueous effluents to rivers and lakes. The largest amounts, containing a large variety of contaminants, are discharged by plants of the pulp-and-paper, petroleum, petroleum processing, and chemical industries. Agriculture is also a source of contaminants since, when irrationally employed, fertilizers and pesticides can get into the water of lakes and streams. As a result, rivers, lakes, seas and the ocean are becoming more and more polluted with petroleum, heavy metals, chlororganic and other organic compounds, radioactive compounds and many other poisonous substances and chemicals. Protection of the ocean is a problem of worry to people all over the world. The ocean is the site of a global process of the earth's "breathing"—of photosynthesis in which a large part of the carbon dioxide in the atmosphere is consumed and more than half of its oxygen is liberated. The death of the plankton, by which this photosynthesis process

is carried out, is detrimental to this exchange of gases between the atmosphere and the ocean. Moreover, the continuing process of pollution of the aquasphere can finally result in the death of all living things in the ocean.

Industrial wastes are also a cause of solids contamination of the soil. Dust and soot from stack gases, sludge formed in industrial processes and in purifying gases (for example, lime sludges) destroy vegetation and result in formation of lifeless areas on the earth's surface.

The chemical industry bears significant responsibility for contamination of both the atmosphere and aquasphere. A characteristic feature of the discharges of the chemical industry is the great variety of the toxic substances. Such substances as chlorine, hydrogen sulphide, carbon monoxide, mercury, phenol, thiophos, DDT, many other metals and organic compounds are especially harmful. A number of these toxic substances are discharged by chemical plants in very large amounts, examples are sulphur dioxide, sulphuric acid mist, nitrogen oxides, chlorine, hydrogen chloride, etc.

The USSR was the first country to develop and introduce regulations governing maximum permissible concentrations of harmful substances in air and water. These levels are compulsory ones for use in designing, building and exploiting industrial plants and also for residential areas. Tables giving the maximum permissible levels (MPL) of harmful substances in the air of the atmosphere and in industrial premises, and also in different kinds of water basins are contained in handbooks. Maximum permissible levels are such which do not adversely affect, directly or indirectly, the health of humans, do not lower a person's ability to work, do not have any negative effect on the way he feels or his spirit. The prescribed norms on which measures for protection of the environment are based make reliable forecasting of probable level of air pollution in residential areas and in the vicinity of industrial plants. Table 20, for an example, gives the MPL values for SO<sub>2</sub> in the air of the atmosphere in the USSR and other countries.

TABLE 20

**Active Effect of Maximum Permissible Concentrations  
of Sulphur Dioxide**

Country	MPL, C mg/m <sup>3</sup>	Period of contact t, min	Active effect, Cτ
USSR	0.5	20	10
West Germany	0.75	30	22.5
USA	4.4	37	162.8

At present environmental protection from industrial discharges is achieved mainly by employing various techniques for purifying gaseous and aqueous plant effluents, which provide levels of contaminants below MPL values. Discharge to the atmosphere and water basins results both in product losses and detriment to the environment. However, almost in all cases there exists a possibility for partial or complete recuperation of discharged matter, i.e. for reprocessing of purification products to return valuable components to the production process.

At the modern level of technological development industrial discharge of waste products to the environment is not inevitable and can be completely avoided. Industrial waste products and the accompanying problems of purifying gaseous and aqueous plant effluents only result from non-scientific, faulty organization of the overall and of individual production processes. The plant of the future will have to operate without harmful discharges, achieved by integral utilization of all the components of the raw materials, by use of closed-cycle production schemas and maintaining optimal values of process variables which result in maximum yield of the desired product. A feature of production processes now under development is the wide use of recycle schemas.

## 2. Removing Harmful Impurities from Industrial Stack Gases

The harmful impurities in industrial gas-phase discharges to the atmosphere can be divided into two groups: (a) suspended particles (aerosols): dust, smoke, mist, and (b) gas- and vapour-phase substances. The first group is made up of suspended solid particles of inorganic or organic origin, and also of suspended liquid particles, which are introduced into the atmosphere with gas-phase technological discharges (purge gases), tail gases, and ventilation system discharges. Inorganic dust in industrial discharges is a feature of processing of metals and their ores, the manufacture of aluminosilicates, various inorganic salts and fertilizers, carbides, abrasives; cement and other inorganic substances. Examples of organic industrial dusts are coal-, wood-, peat-, shale-, flour-, and carbon-black suspensions. Industrial mists in the stack gases is a characteristic feature mainly of the manufacture of acids, primarily of sulphuric and phosphoric acids, and of their concentrations. The particle size of dusts and mists varies widely—from tens of microns to several hundred microns.

The second group—gas- and vapour-phase impurities—is more numerous. It is made up of acids, halogens and halogen derivatives, gaseous oxides, aldehydes, ketones, alcohols, hydrocarbons, amines, pyridines, mercaptanes, vapours of metals and many other gas-phase components of industrial stack gases. The need to eliminate gas-phase industrial product discharges or to at least subject the dis-

charges to a high degree of purification arises not only from their harmful effects on health, vegetation and animal life. Discharge of industrial products to the atmosphere is a cause of significant economic loss since large amounts of valuable products are irretrievably lost in this way—organic solvents, metals, sulphur dioxide, etc. Thus, the loss of sulphur in stack gases exceeds the amounts consumed in manufacturing sulphuric acid in industrially developed countries. Figures for 1965 are given below.

	<i>Sulphur lost,</i> million tons	<i>Sulphur consumed,</i> million tons
USSR	8.9	~ 6
USA	12.2	~ 9
Great Britain	3.2	2.5
West Germany	1.7	1.2

Another factor is that chemicals in the air are the cause of premature corrosion of metals; in industrial areas steel rusts at a rate of 3 to 4 times above that for farming areas. The most radical way to protect the atmosphere from harmful industrial contaminants is by providing rational organization of new industrial processes and improving existing ones so as to completely exclude, or at least to reduce to a minimum the discharge of harmful gas-phase effluents. The most important method in organizing no-waste schemas is the use of recycle flow schemes for the overall- and for individual processes, and also the integral utilization of the starting materials and by-products on which new processes are based. Thus, the utilization of the sulphur dioxide discharged to the atmosphere by non-ferrous metallurgy plants as a raw material for manufacturing sulphur dioxide removes this source of environmental pollution and yields a valuable product, sulphuric acid, at a cost 30% below that of the older methods, used in the chemical industry. A classical example of a recycle process with no discharge of waste gases to the atmosphere is that of ammonia synthesis.

The current level of development of science and technology cannot as yet completely eliminate discharge of toxic substances to the atmosphere. Because of this, an available method of protection—various gas purifying units—must be used. The function of such a unit is to reduce the concentration of pollutants to below the maximum level permitted by sanitation laws. If the MPL cannot be reached by purging the gas it must be subjected to manifold dilution or discharged through a very tall stack to disperse the impurities in the upper layer of air. For the determination of the pollutant content at ground level as a function of the stack height and other factors by theory the effects of turbulent diffusion must be taken into account but no method for the calculations has been developed. The necessary stack height is found using empirical formulas, such

as

$$C_m = \frac{235 \cdot G_m}{2.5 w_0 H^2} \quad (11.1)$$

where  $C_m$  is the maximum concentration of the pollutant at breathing height—1.8 m above ground level, milligrams/m<sup>3</sup>;  $G_m$  is the amount of the pollutant being discharged to the atmosphere gram/sec;  $H$  is the stack height, m;  $w_0$ —wind velocity at 10 m above ground, m/sec.

Formula (11.1) can be used for determining permissible discharge of a pollutant at a given stack height. Thus, if  $H = 100$  m the permissible level of SO<sub>2</sub>, 0.5 mg/m<sup>3</sup>, will be reached if the SO<sub>2</sub> discharge is 15 tons per day. Modern supersize heat power-plants have  $G_m$  values as high as 1500 tons per day SO<sub>2</sub>. To reach the sanitation regulations level removal of SO<sub>2</sub> from the gas discharge should be 99% effective, which is the limit of what a modern purification unit can do. It follows that even if there is a very efficient purification building a tall stack is a necessary additional precautionary measure. In industry the required level of purification, called for by sanitation regulations, is generally reached using several stages of purification with different process conditions maintained and occasionally using different methods of purification.

The gas-purification methods used depend on the nature of the pollutants and they can be divided into methods for removing aerosols and for removing gas- and vapour-phase impurities. The method used depends mainly on the physicochemical properties of the impurities, their composition, phase state, particle size, etc. The great diversity of the harmful impurities in industrial gas discharges demands that a large variety of techniques and reactants be employed for purification. Table 21 contains a classification and short descriptions of the most widely used methods for removing aerosols from gases. Removal of gas- and vapour-phase impurities from gases is a typical feature of chemical industry and is widely used at chemical plants. The methods used for purging industrial gas discharges of gas- and vapour-phase impurities can be divided into 3 groups: (1) absorption with liquids; (2) adsorption by solids and (3) catalytic purification.

**Absorption with liquids** is the method used on the broadest scale and until now the most reliable method for gas purification. It is the basic method used in industry for removing carbon dioxide and monoxide, nitrogen oxides, chlorine, sulphur dioxide, hydrogen sulphide and other sulphur compounds, acid vapours (HCl, H<sub>2</sub>SO<sub>4</sub>, HF), cyanide compounds, various toxic organic compounds (phenol, formaldehyde, phthalic anhydride and others), etc. The absorption methods are based on selectively dissolving pollutants in a liquid (physical absorption) or selectively removing them by means of a reaction with an active component of the sorbent (chemisorption).

Absorption purification is a continuous process and, usually, a cyclic one, since the process of absorption of impurities is usually accompanied by regeneration of the solvent (by heating or reducing the pressure) and its return to the head of the purification cycle. This is accompanied by desorption of the absorbed gas component, which is obtained in a concentrated form (see Part I, Fig. 128).

Elements of design calculations of absorption and chemisorption processes were given in Part I, Chapter 5. The principal technological indexes of absorption purification—degree of purification (efficiency)  $\eta$  and the mass-transfer coefficient  $k$ —depend on the solubility of the gas, the values of the process variables in the reactor ( $T$ ,  $P$ ,  $w$ ) and other factors, such as the equilibrium and reaction rate of chemisorption. If there is a reaction in the liquid phase the value of  $k$  will be larger than for physical absorption. In chemisorption the equilibrium ratios differ sharply from those for physical absorption by the liquid and, consequently, also the effect of the equilibrium on the driving force. In the limiting case, that of an irreversible reaction in the liquid phase (neutralization), the compound formed has practically zero partial vapour pressure over the liquid. However, a chemisorption process in such a case can not be of the recycle type (the solvent cannot be returned to the head of the purification process) and its use is advisable only if the solution obtained can be utilized in some other way. Most of the chemisorption processes employed in industry are based on a reversible, exothermic reaction and when the solution is heated the newly formed compounds dissociate and liberate the initial substances. This is the technique on which regeneration of the chemisorbents in recycle schemes is based; heating is essential since the capacity of a chemisorbent depends very little on the pressure. Chemisorption processes are especially suited for fine purification of gases containing comparatively small amounts of impurities.

A large variety of liquids are employed as solvents for purifying gases and they are assessed using the following indexes: (1) absorption capacity (i. e. the solubility of the basic impurity) as a function of pressure and temperature. The value of this index determines the cost of purification, i. e. the number of necessary stages, energy consumption for recycling, energy consumption for desorption of the gas, etc. In the desorption method solvents with a large coefficient of temperature change in solubility,  $K_{t+10}/K_t$  are needed; (2) selectivity, which is described by the ratio of the solubilities of the gases being separated, and also by their relative rates of absorption (the larger the difference in the values of these indexes, the higher will the selectivity be); (3) the vapour pressure of the solvent, which should be minimal so that contamination by solvent vapours of a gas being purified be as small as possible; (4) low cost; (5) corrosion of apparatus, which should be at a minimum.

Methods Used for Removing Aerosols from Industrial Stack Gases

Collection method	Short description	Collection equipment	Industrial-use data
<b>A. Mechanical methods</b> <b>1. Dry methods:</b> Gravitational dust separation	The method is based on settling of dust particles by force of gravity from a dust-containing gas stream with a low rate of flow without changes in the flow direction. The method has low efficiency, is employed only for preliminary, rough purification of a gas and is being replaced by more efficient methods of gas purification	Dust-setting gas lines and settling chambers	To facilitate dust removal vertical partitions which reduce the flow rate are added. The capacity of a gravitational apparatus, $\pi = Sw_0$ (where $S$ is the area of the horizontal cross section of the apparatus and $w_0$ the settling rate), does not depend on its height, and because of this a large number of horizontal partitions are built into the chamber at a distance of 40-100 mm apart so as to divide the gas into a corresponding number of flat streams
Inertial dust separation	The method is based on forces of inertia, i. e. on the tendency of a particle to continue to travel in the original direction of flow following a change in the direction of a gas stream. The method has low efficiency and can be employed only for rough purification of a gas with low initial dust content	Baffle impingement separators. Inertial dust separators with a packing of cone-shaped rings	The pressure drop: $\Delta P = 10-40$ mm $H_2O$ (100-400 Pa). The rate of flow at the inlet is $w_g = 10-15$ m/sec. Separates particles of size $d > 20$ microns. Gratings often clog up and suffer wear. Is employed for a gas with an initial dust content of not over 1.5 g per cu m. Separation efficiency depending on the particle size, is from 20 to 70%
Centrifugal force dust separation	The method is based on the centrifugal forces created when the gas stream being cleaned rotates inside the col-	Cyclones and batteries of cyclones. Rotary dust	Cyclones with large gas stream capacities (over 200 000 cu m per hr) provide fairly good separation of parti-

Filtering

lection equipment or by rotating parts in the equipment (for example, a rotor in a stationary casing). Widely used for medium and rough separation of suspensions from gases

Based on passing the gas being cleaned through various kinds of filtering fabrics (cotton, wool, synthetic fibre) or other materials—ceramics, metal-ceramics, but most often through specially-made-fibre fabrics (asbocellulose, wool or cotton plus asbestos, glass fibre, etc.). Employed for fine gas cleaning. Positive features are low cost equipment and high collection efficiency. Negative features are large pressure drops and rapid clogging

collectors (rotocloners, mechanical scrubbers)

cles with  $d > 30$  microns. For  $d = 5$  microns particles  $\eta = 80\%$ , and for  $d = 2$  microns particles  $\eta < 40\%$ . The overall pressure drop of a high capacity cyclone is  $\Delta P = 100 \text{ mmH}_2\text{O}$  (4000 Pa). Usually  $\Delta P/\rho_t = 55\text{--}75 \text{ mmH}_2\text{O}$  (550-750 Pa), where  $\rho_t$  is the gas density at operating conditions

Fabric filters (including bag filters)

In industry bag filters made of wool, synthetic fibre and cotton cloth are used. The maximum permissible temperature of the gas being cleaned is  $60\text{--}65^\circ\text{C}$ . The filtering rate is low— $0.1\text{--}1.5 \text{ m/min}$ . Collection efficiency is  $85\text{--}99\%$  depending on the particle size and initial dust content.  $\Delta P \cong \cong 100 \text{ mmH}_2\text{O}$ . Energy consumption amounts to approximately  $1 \text{ kWhr}$  per  $1000 \text{ cu m}$  gas at standard conditions

Fibre filters

Operate with high efficiency amounting to  $99.5\text{--}99.9\%$  dust collection at  $w_g = 9\text{--}10 \text{ m/sec}$  and  $\Delta P = 50\text{--}100 \text{ mmH}_2\text{O}$  (500-1000 Pa). If a glass-fibre filtering material is used gases with temperatures up to  $275^\circ\text{C}$  can be cleaned. For fine cleaning at higher temperatures ceramic or metal-ceramic filters are used



Table 21 (Continued)

Collection method	Short description	Collection equipment	Industrial-use data
2. Scrubbers	The method is based on scrubbing the gas with a liquid, usually water, with maximum possible area of contact and intensive mixing of the gas being cleaned and the liquid. Employed for separating particles of dust, ash and mists of all sizes and is the most widely used and most reliable method for use as the final stage of mechanical gas purification. A negative feature is the large volume of liquid waste (sludge) formed	Packed towers (scrubbers)	Distinguishing features are simple design, ease and stability of operation, low-pressure drop ( $\Delta P=30\text{-}80\text{ mmH}_2\text{O}$ ). For these reasons it is used on a broad scale. Efficiency of a single stage does not exceed 70-85%, and because of this scrubbers are employed for precleaning suspensions. At high dust concentrations tend to clog
		Cyclone scrubbers (centrifugal scrubbers)	Can be used with advantage for cleaning large volumes of combustion products, since the apparatus has high capacity (at $D=1\text{ m}$ cleans up to 20 000 cu m of gas per hr), low pressure drop (40-80 mmH <sub>2</sub> O) and high dust collecting efficiency ( $\eta=93\text{-}99\%$ , depending on particle size)
		Froth scrubbers	Operate at high intensities with flow rates of the gas of 1-3 m/sec referred to the apparatus cross section. Have high capacity at relatively low pressure drops ( $\Delta P$ approximately 60 mmH <sub>2</sub> O per stage). Collect 98-99% of dust particles (or mists) of size over 5 microns and 75-80% of size under 5 microns. An apparatus has 1 or 2 trays. Employed for separating suspensions of diverse particle size

<p><b>B. Electrostatic method</b></p>	<p>The method is based on ionization and giving the suspended dust particles an electric charge by passing the gas through a high tension field created by discharge electrodes. The particles separate from the gas onto grounded collecting electrodes. For removing mists liquid film precipitators are employed. Electrostatic separation is one of the best ways of removing dusts, which combines simple design, low pressure drop and high gas capacity with high collecting efficiency. The method is a universal one, i. e. it can be used for all types of dust of diverse particle size. A negative feature is the high cost of construction of the collection equipment and electric energy consumption</p>	<p>Venturi scrubber</p>	<p>An efficient apparatus which operates at throat velocities of 100-120 m/sec. Efficiency of mist collection is 99-100%, dust particles <math>d=0.01-0.35</math> micron is 50-85%, <math>d=0.5-2</math> microns is 97%. A negative feature is a large pressure drop which for dust collection amounts to 230-280 mmH<sub>2</sub>O and for mist collection to 760 mmH<sub>2</sub>O</p>
<p></p>	<p>Electrical precipitators</p>	<p>Operate at voltages on the discharge electrodes of 25-100 kW and can be used over a wide range of gas temperature (from -70 to 500 °C) and pressures. <math>\Delta P</math> does not exceed 10-15 mmH<sub>2</sub>O. Energy consumption is 0.2-0.3 kW/hr per 1000 cu m of gas cleaned. Efficiency exceeds 90% and can be as high as 99.9% in multifield precipitators under optimal operating conditions and partial size not below 1 micron</p>	<p></p>

The principal sorbents used in cleansing tail gases are water, ammonia water, solutions of caustic soda and carbonates, ethanolamines, potassium manganate and permanganate, suspensions of calcium hydroxide, manganese oxides, etc. The absorber-reactors used are towers (packed towers and spray towers), tray and shelf reactors (bubble towers, multitray froth absorbers), Venturi scrubbers. The most widely used, a universal type of scrubber, is the packed tower, which is employed on a wide scale for removing nitrogen oxides,  $\text{SO}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{Cl}_2$ , vapours of metals (mercury) and other impurities from gas streams. Its salient features are simplicity of design and operation and operating stability. However, the rate of mass transfer is not very high due to the low intensity of the process variables of scrubbers, which operate at  $w_g$ -values of 0.02-0.7 m/sec. As a result the tower volume is large and the unit is far from compact.

More intensive operation is characteristic for froth absorbers and Venturi scrubbers. Froth absorbers, for example, operate at  $w_g = 1.0$ -3.0 m/sec and provide a comparatively high rate of absorption and desorption, and as a result their size is several times smaller than that of packed towers. The degree of purification grows with the number of trays in the apparatus and in some processes it is as high as 99%. General positive features of absorption purification are that the process is a continuous one, that large quantities of impurities can be separated from a gas stream, and that the solvent can be continuously regenerated in a recycle scheme. Drawbacks are the large size of the equipment (for example, scrubbers), the complexity and multistage nature of the flow schemes, since to achieve a high degree of purification and complete regeneration of the solvent large volume equipment and a number of purification stages are necessary.

**Adsorption by solids** is based on the selective separation of harmful impurities from a gas stream using adsorbents—solid granular materials with a very large specific surface area. In purifying gases both physical adsorption, based on Van der Waals forces of attraction, and chemisorption are employed. The adsorbents used are very porous materials, usually activated carbon, silicagel or synthetic zeolites (molecular sieves). Most important are the adsorption capacity of a sorbent, its activity, selectivity, thermal stability, length of service without changes in structure or surface properties, ease of regeneration and low pressure drop across a bed of the sorbent. Activated carbon of various grades and silicagel have a long record of successful service in industry.

Synthetic zeolites—aluminosilicate crystalline substances with uniform pore-size—are very important in gas purification. Depending on the ratio between  $\text{Si}^{4+}$  and  $\text{Al}^{3+}$  ions in the crystal lattice zeolites differ in their lattice structure, distribution and charge of the cations. These sorbents satisfy the requirements of gas purification proc-

esses very well: they have high sorption capacity, and high selectivity for components of a gas mixture (especially for polar- and aliphatic-compounds) even when their content is very low.

Adsorption of gaseous impurities is carried out mainly in batch type reactors without heat exchange devices and with the sorbent on trays. Usually the gas being purified flows downward through the adsorbent bed at a rate limited by the pressure drop, from 0.05 to 0.3 m/sec. As the process continues the activity of the sorbent decreases as the surface becomes saturated with the substance being adsorbed and also covered with foreign substances—dusts, tars, etc. The saturated sorbent is regenerated by heating and passing steam, or superheated steam, air or an inert gas (nitrogen) through it. In some cases the sorbent which has lost its activity is completely replaced. When small amounts of a toxic substance are removed from air ( $2\text{--}5 \cdot 10^{-4}$  volume percent) or air is deodorized by adsorption, installations are used consisting of cells with replaceable perforated cartridges containing activated carbon. The service period of the cartridges is measured in years and when replaced they are discarded, or occasionally regenerated.

Most promising is a continuous recycle process for purification of gases by adsorption, which can be carried out in towers with a moving or suspended (fluidized bed) adsorbent which circulates through an adsorber and a regenerator. A basic advantage of purification of gases by adsorption is that it is possible to process huge volumes of a gas with relatively small amounts of the adsorbent and achieve a high degree of purification. This is due to the high sorption capacity of industrial adsorbents even at low partial pressures of the impurities being separated. Because of this the method is especially effective for removing impurities contained in a gas stream in low concentrations, for example for fine separation of organic sulphur compounds and mercury vapours, for gas deodoration. An important industrial application is adsorption of vapours of organic solvents from gas streams using activated carbon, which has high selectivity with respect to organic compounds. The process is widely used for removing and recovering organic solvents from gas streams.

Drawbacks of adsorption methods for purifying gases are the batch nature of the process, the low operating efficiency of batch-process reactors, and the high cost of adsorbent regeneration. The continuous process of gas purification by adsorption removes these negative features but for its use high-strength sorbents are needed, which for most applications have not yet been developed.

**Catalytic gas purification** is based on catalytic reactions by which pollutants are converted into other compounds. Thus, the catalytic method differs from those described above in that toxic substances are not separated from the gas stream, but are converted into compounds whose presence in the atmosphere is permissible, or into com-

pounds which can easily be separated from the gas. In the latter case an additional purification stage is necessary—either of absorption or adsorption. For purifying gas streams heterogeneous catalysis, over a solid catalyst, is employed almost exclusively (see Part I, Chapter 6). Catalytic oxidation of toxic organic substances and carbon monoxide at low temperatures, i.e. without preheating of the gas (or air) being purified, is the most widespread of the processes. Catalytic removal of toxic oxides and sulphide compounds is also carried out by hydrogenation; thus, by selective hydrogenation CO is converted to  $\text{CH}_4$  and  $\text{H}_2\text{O}$ , nitrogen oxides to  $\text{N}_2$  and  $\text{H}_2\text{O}$ , etc.

The most important of the positive features of the catalysis technique is the possibility of achieving a very high degree of gas purification—in some cases as high as 99.9%. The limiting value of the remainder of impurities in the gas depends mainly on the reaction equilibrium. Under industrial conditions (at 100-500 °C) the equilibrium constants of the reactions on which removal of the impurities is based are usually very high and the reactions are practically irreversible. Because of this the remainder of toxic impurities in the gas is generally very low and does not exceed the MPL.

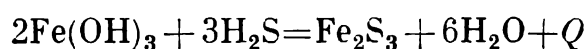
A drawback of catalytic purification is that new substances are formed which must in some cases then be removed by absorption or adsorption techniques. This has a very negative effect on the economics of the process. The selection of a method for removing toxic gases or vapours is based on the specific conditions of the given industrial process. The purification economics becomes better if waste products are employed as the purifying reactants (adsorbent, absorbent, catalyst) and also when valuable products are recovered from stack gases, for example vapours of benzene or other solvents, mercury or other metals, etc. Generally, the concentration of the impurities in industrial waste gases is low and their volume is very great and because of this the purification units are large and complex, and the process does not pay for itself.

All the methods discussed above are costly. The higher the necessary degree of purification as determined by sanitation regulations, the larger the purification unit becomes. For example, in manufacturing nitric acid in order to lower the content of nitrogen oxides from 0.25 to 0.05% by volume using absorption with water in packed towers (at  $P = 3.5\text{--}4$  atm), i.e. to increase the absorption efficiency from 97.5 to 99.5%, the volume the absorbers must be doubled. The permissible concentration of NO in air fixed by sanitation regulations is 0.1 mg/m<sup>3</sup> and to reach this level very effective purification techniques must be employed, for example, catalytic purification. By catalytic hydrogenation of nitrogen oxides their remainder can be brought down to 0.001% (vol), which is close to the MPL. However, the use of a catalytic hydrogenation unit raises the cost of the nitric acid by 10 to 12%. Any gas purification process is best carried out in

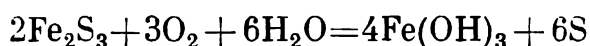
continuous operation high-intensity apparatus in all respects—and also in respect to the processing costs. Examples of such apparatus are froth scrubbers and Venturi scrubbers for absorption and reactors with a moving or a fluidized bed of adsorbent or catalyst for use in the corresponding processes.

For comparing purification methods and their technical-and-cost indexes removal of hydrogen sulphide from a gas will be discussed. Absorption, adsorption and catalytic techniques are used to remove this toxic substance from gas streams. In absorption purification of the hydrogen for ammonia synthesis  $\text{H}_2\text{S}$  is absorbed using ethanolamines or soda-arsenic solution. For removing  $\text{H}_2\text{S}$  from stack gases occasionally less expensive solutions are employed, such as alkaline metal carbonates or ammonia in water, suspensions of calcium hydroxide, iron (III) hydroxide in a soda-ash solution (iron-soda solution), etc. In all these cases there is a chemical reaction in the liquid phase which promotes the process rate and  $\text{H}_2\text{S}$ -removal efficiency. The used sorbents must be regenerated to avoid contamination of the water basins. All the absorption purification units, which are made up of packed towers, operate at low temperatures of 20 to 30 °C and either atmospheric or elevated (up to 30 atm) pressures. Chemisorption is accompanied by a stage of desorption regeneration of the solvent (using heating or distillation under vacuum to separate hydrogen sulphide at a higher concentration, which is utilized for manufacturing sulphuric acid). In the arsenic-soda process the products of regeneration are sulphur and sodium thio-sulphate. A schematic flow diagram of the arsenic-soda purification process for removing hydrogen sulphide from gases is given in Fig. 116.

For dry sorption of hydrogen sulphide from tail gases usually a body based on oxides of iron, zinc, copper, or manganese is employed. In recent years synthetic zeolites have come into use. Sorption of  $\text{H}_2\text{S}$  by the purification body and regeneration of the adsorbents are accompanied by chemical reactions. For example, in purification employing an ironoxide body the active component of the sorbent is ferric hydroxide.



Regeneration of the purification body is carried out periodically by passing a mixture of air and steam through it.



Purification is carried out in multitray adsorber towers with a bed of the purification body on each tray. A continuous recycle process with purification at high temperatures in a fluidized bed of oxides of iron and manganese is now being used; oxygen in air is added to the gas being purified and the sulphur content of the sorbent is

maintained at a 10%-level by continuously circulating it through the adsorber and a regenerator (see Part I, Fig. 116). When a stationary bed is employed purification is carried out at 25-30 °C, whereas for a fluidized bed the temperature is 300-400 °C, which results in a sharp rise in the rate of the chemical reactions.

Separating H<sub>2</sub>S from a gas using synthetic zeolites is based on physical adsorption. Purification is carried out at 20-25 °C and 3 atm in a unit consisting of several towers packed with the sorbent. Regeneration is carried out at 300-350 °C; the H<sub>2</sub>S is desorbed in

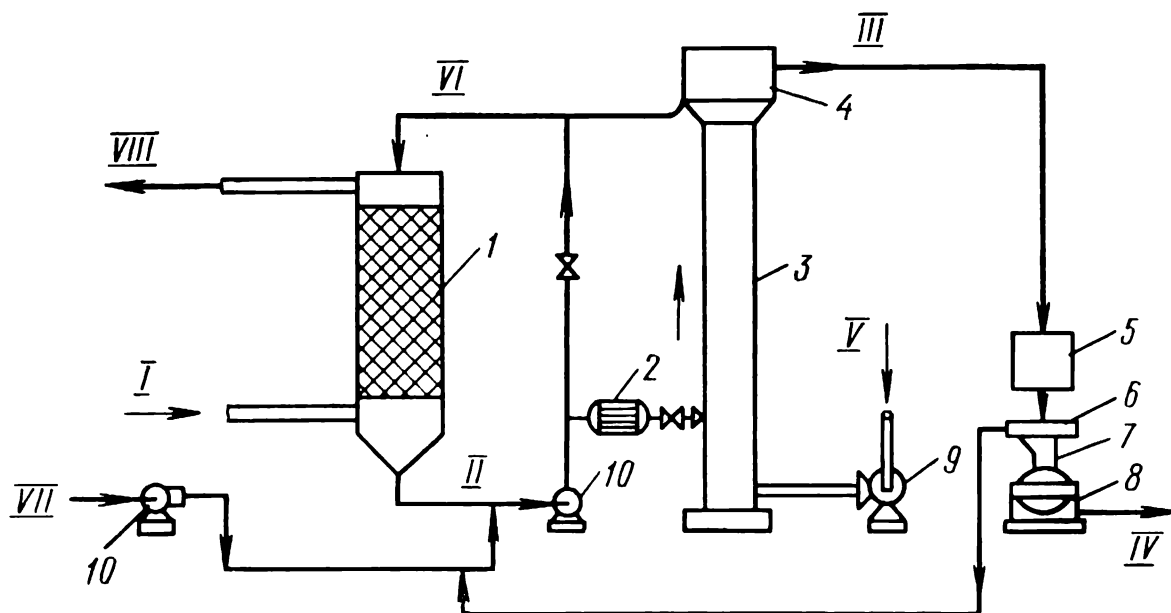
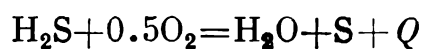


Fig. 116. Flow diagram of a unit for removing hydrogen sulphide from a gas by absorption (arsenic-soda process):

1—packed absorption tower; 2—solution heater; 3—regenerator; 4—separator; 5—sulphur-foam collector; 6—filter; 7—hopper for sulphur removed by filtering; 8—autoclave; 9—air blower; 10—pump. I—gas, to purification; II—solution, to regeneration; III—sulphur foam; IV—sulphur; V—air; VI—regenerated solvent; VII—fresh arsenic-soda solution; VIII—purified gas

a stream of a chemically inert gas or of a gas containing SO<sub>2</sub>. In this latter case the catalytic effect of the zeolite results in formation of vapour-phase sulphur, which is condensed. Of the catalytic processes for removing H<sub>2</sub>S and other sulphur compounds from a gas the most popular is H<sub>2</sub>S-oxidation by the reaction



over activated carbon as the catalyst. Steam and ammonia (about 0.2 g/m<sup>3</sup>) are added to the gas being purified to promote catalysis. The process is carried out in multitray, plug-flow reactors without heat exchange devices (see Part I, Fig. 100). Catalyst activity drops as the pores become filled with sulphur and when the weight of the

latter reaches 70 to 80% of the weight of the carbon the catalyst is subjected to regeneration by washing it with an ammonia sulphide solution. The ammonia polysulphide solution produced is decomposed by introducing direct steam to form liquid sulphur. However, with use the carbon loses its activity due to accumulation of tarry deposits and it must be replaced. The adsorption temperature should not exceed  $50^{\circ}\text{C}$  since the reaction is exothermic. The catalytic removal of  $\text{H}_2\text{S}$  process can be improved by carrying out oxidation in a fluidized bed of activated carbon and its continuous regeneration.

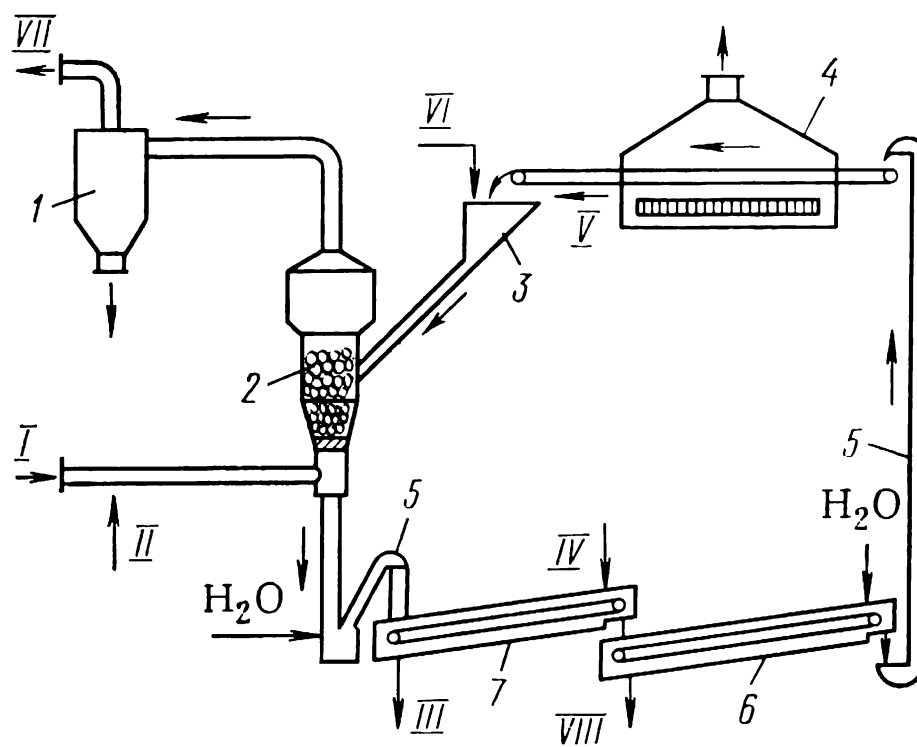


Fig. 117. Flow diagram of catalytic hydrogen-sulphide removal in a fluidized bed of activated carbon:

1—cyclone dust collector; 2—fluidized-bed reactor; 3—hopper with a feeding device; 4—drying chamber; 5—lift; 6—carbon scrubbing reactor (worm screw); 7—sulphur-extraction reactor (worm-screw dissolver). I—gas, to purification; II—air with an admixture of ammonia; III— $(\text{NH}_4)_2\text{S}_n$ -solution, to regeneration; IV— $(\text{NH}_4)_2\text{S}$ -solution; V—regenerated carbon; VI—fresh carbon; VII—purified gas; VIII—wash water

Because in a fluidized bed heat can be removed at a high rate there is no limit on the initial  $\text{H}_2\text{S}$  concentration of the gas. The production capacity of a fluidized bed reactor is 6 to 8 times higher than that of one with a stationary bed and its size is correspondingly smaller; operation can be converted to full automatic control. Fig. 117 is a flow diagram of catalytic  $\text{H}_2\text{S}$ -removal in a fluidized bed of activated carbon. Some of the process indexes of the methods for removing  $\text{H}_2\text{S}$  from gas streams described above are given in Table 22.

A comparison shows that the dry processes—sorption and catalytic ones—provide a higher degree of  $\text{H}_2\text{S}$ -removal at lower values of the consumption indexes.





### 3. An Example of Design Calculations of a Reactor for Gas Purification

As an example of the design calculations of a reactor with mass transfer for removing pollutants from a process tail gas, the principles on which the designing of a froth absorber operating at close to complete mixing is based are considered below. Reactors of this type can be employed for separating aerosols, and gas- or vapour-phase pollutants from a gas stream. In the latter case froth apparatus of a multitray type are used. The design calculations of a multitray apparatus consist essentially in determining the required interface area and required number of trays. The values can be calculated if the mass-transfer coefficient,  $k_m$  or the tray efficiency  $\eta$  is known. Values of  $k_m$  or  $\eta$  are determined by experiment for various systems as a function of the hydrodynamics conditions and the physicochemical features of the system. A number of dimensionless-group equations, used for calculating  $k_m$  and  $\eta$  were given in Part I.

The scheme of the calculations:

1. The superficial rate of gas flow in the apparatus is selected. In doing so one should take into account the limits of the flow rate (1 and 3 m/sec\*) and possible deviations from design rate in the absorber operation conditions, so that these limits are not exceeded. For absorption of high-solubility gases the rate should be nearer to the upper limit, for low-solubility ones—to the lower limit.

2. The cross-sectional area of the apparatus is found. The cross-sectional area ( $m^2$ ) is

$$S = \frac{V_g}{w_g} \quad (11.2)$$

where  $V_g$  is the volumetric flow rate at the entrance to the absorber under operating conditions,  $m^3/sec$ . The maximum permissible size of an apparatus is limited by its ability to provide uniform gas flow over the cross section. For single-tray apparatus the maximum permissible size is usually 5-7  $m^2$ .

3. Calculation of the flow rate of the liquid fed to the sieve plate is carried out in different ways depending on the operating conditions and the function of the apparatus. In all cases a material balance of the froth absorber must be drawn up.

4. The required number of plates is calculated using the known value of the mass-transfer coefficient  $k_m$  or of the tray efficiency  $\eta$ . Definitions of these parameters were given in Part I, Chapters 2

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\* In new type of froth equipment containing a ball packing the gas rate can be as high as 5 m/sec.

and 5. The total mass-transfer area is found from

$$F = G/(\Delta C_m k_m \tau) \quad (11.3)$$

where  $\Delta C_m$  is the mean driving force of mass transfer (see Part I, Chapter 2) and  $G$  is the total amount of the substance transferred from one phase to another (retained in the froth apparatus). The number of plates in the froth apparatus is  $n$ :

$$n = F/S \quad (11.4)$$

where  $S$  is the area of a plate. The number of plates in a froth apparatus can be determined (or checked) using the relationship between the overall efficiency of the apparatus  $\eta$  and the efficiency of a single plate  $\eta_p$ :

$$n = \frac{\log(1 - \eta)}{\log(1 - \eta_p)} \quad (11.5)$$

5. The specific flow rate of the liquid across the plate and the height of the weir are determined as follows. The depth of the froth-bed on a plate depends on the rate of the gas flow, the specific flow rate of the liquid and the weir height. The specific liquid flow rate is

$$i = L/b \quad (11.6)$$

where  $L$  is the volumetric flow rate,  $\text{m}^3/\text{hr}$  and  $b$  is the downcomer length, m. The length of the downcomer is usually taken as the length of an arc of the segment with a chord of about one-third of the diameter. Having found  $i$  and knowing  $w_g$  one can calculate the depth of the liquid bed,  $h_0$ , using

$$h_0 = H/(806 w_g^{0.5}) \quad (11.7)$$

Equation (11.7) is used for an air-water system. For other G-L systems  $h_0$  is calculated using empirical equations of the type

$$H = a \cdot w_g (h_0 + b) + c h_0 \quad (11.8)$$

where  $a$ ,  $b$  and  $c$  are constants whose values depend on the physical properties of the liquid. For example

	$a$	$b$	$c$
for water	0.65	0.015	2.00
for $\text{Na}_2\text{CO}_3$ solutions	0.40	0.063	1.80
for $\text{H}_2\text{SO}_4$ solutions	0.70	0.012	1.75
for $\text{NaOH}$ solutions	0.25	0.100	2.00

The height of the weir  $h_w$  (m) is found from

$$h_w = \frac{H (h_0^{0.6} - h_1^{0.6})}{h_0^{0.6}} \quad (11.9)$$

where  $h_1$  is the height of the layer of liquid in the froth above the weir and

$$h_0 = (3.15 + 0.005i) \sqrt[3]{i^2} \quad (11.10)$$

In calculating  $h_0$  and  $h_w$  from equations (11.7) and (11.9) an assumed height of the froth layer  $H$  is used.

6. The tray parameters, i.e. the hole size,  $d_h$ , and the distance between the centres,  $m$ , are found. At first, the shape of the perforations is selected; the selection is based on the method to be used for manufacturing the plates. The width of slots,  $d_s$ , or the diameter of circular holes,  $d_h$ , are usually selected at  $d_s = 3-4$  mm, or  $d_h = 4-6$  mm. Then for a rate of gas flow through the perforations,  $w_h$ , of between 6 to 13 m/sec the free area of the grid,  $S_h$  (per cent), is found from

$$S_h = (w_g \cdot 100) / (w_h \cdot \varphi) \quad (11.11)$$

where  $\varphi$  is the ratio of the part of the tray with perforations to the apparatus cross section. If external downcomers are used,  $\varphi$  is usually 0.9-0.95, since from 5 to 10% of the cross section is occupied by the tray supports and the unperforated part near the downcomer. The distance between hole centres  $m$  is calculated by means of the formula

$$m = d_h \sqrt{\frac{91}{S_h}} \quad (11.12)$$

with the holes located at the apexes of equilateral triangles.

7. The total pressure drop of a froth absorber (mmH<sub>2</sub>O) is

$$\Delta P_{\text{total}} = n (\Delta P_1 + \Delta P_2) + \Delta P_3 \quad (11.13)$$

where  $n$  is the number of plates in the froth absorber;  $\Delta P_1$  is the pressure drop across the dry plate, mmH<sub>2</sub>O (Pa);  $\Delta P_2$  is the pressure drop due to the froth bed on a tray, mmH<sub>2</sub>O (Pa), and  $\Delta P_3$  the pressure drop across the column inlet, outlet and spray separator, mmH<sub>2</sub>O (Pa).  $\Delta P_3$  comes to approximately 20 mmH<sub>2</sub>O (200 Pa). The pressure drop across a plate 4-7 mm thick is found from

$$\Delta P_1 = 1.45 \frac{\rho_g \cdot w_h^2}{2g} \quad (11.14)$$

where  $\rho_g$  is the gas density, kg/m<sup>3</sup>;  $w_h$  the gas flow rate in the tray perforations;  $g$ —acceleration by force of gravity. If the tray thickness is either increased or decreased, the pressure drop will be 1.2 to 1.7 times larger. The pressure drop in the froth bed is found using the empirical correlation

$$\Delta P_2 = 0.85 h_0 \cdot \rho_1 + 15 \quad (11.15)$$

where  $\rho_1$  is the liquid density, kg/m<sup>3</sup>.

#### 4. Industrial Waste Waters and Methods Used for Purifying Them

Industrial aqueous discharges can be classified either according to their origin, i.e. by branches of industry, or according to their composition. Table 23 lists the branches of industry which discharge

TABLE 23

##### The Principal Toxic Impurities in Industrial Aqueous Discharges

Source of discharge	Principal impurities
Petrochemical and petroleum refining industry	Petroleum, petroleum products, naphthenic acids, mercaptans, phenols, hydrogen sulphide
Coke-chemical industry	Phenols, pyridine bases, tars, hydrocarbons, fatty acids, ammonia
Pulp-and-paper industry	Lignosulphonic acids, mercaptans, sulphites, alcohols, aldehydes, ketones, suspended organic matter
Dyestuffs	Inorganic acids ( $\text{HNO}_3$ , $\text{H}_2\text{SO}_4$ ), nitrocompounds, amines, phenols, dyestuffs
Manufacture of synthetic rubber	Alcohols, hydrocarbons, aldehydes, ketones
Chlorine industry	Chlorine, chlorides, mercury

the largest volumes of dangerous toxic substances in their aqueous effluents. Maximum permissible levels of toxic substances in liquid discharges as fixed by sanitation regulations in the USSR (MPL) are ( $\text{mg}/\text{dm}^3$ ): inorganic acids ( $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ ,  $\text{HCl}$ )—approximately 30; phenol—0.002; tars—20-50; mercaptans—2 to 5; hydrogen sulphide—1 to 3; mercury—0.005; naphthenic acids—0.3, etc. However, it should be remembered that even in these small permitted levels the toxic substances are not absolutely harmless for plant and animal life.

The effect of aqueous discharges on the waters to which they are discharged depends on the composition and physicochemical properties of the impurities. According to this aspect, aqueous effluents can be divided into two groups: (a) those containing inorganic impurities, including such which have a specific toxic nature; (b) those containing organic impurities, including toxic one. The first group is made up of effluents of soda-ash, sulphuric-acid, nitrogen-fertilizer, metallurgical, ore beneficiation, etc. plants. The principal impurities are acids, alkalis, inorganic salts, sulphur compounds, ions of the heavy metals, etc. These impurities increase the salts content of the water to which they are discharged, change its properties—transparency, colour, odour, taste, pH, hardness—and poison living

matter, form insoluble deposits at the bottom, i.e. contaminate the aquasphere.

The liquid wastes of the second group are discharged by petrochemical, fuel-carbonization, pulp-and-paper, organic-synthesis and many other plants. The contaminants in the effluents of such plants are of especially great harm to plant and animal life. The effects of these pollutants on water basins and the surrounding territory are very diverse. Most of these organic impurities are subject to oxidation for which they consume the oxygen dissolved in the water. This results in a deficiency of oxygen which must be present for living matter to exist. Because of this, in water purification the principal index of purification efficiency is that which describes the content of organic matter in the water which can decompose and be oxidized—the biological oxygen deficiency (BOD). The BOD is defined as the amount of oxygen expressed in mg per litre (or g per m<sup>3</sup>), which the unstable organic impurities remove from the water over a given period of time. Depending on the period the index is given as BOD<sub>1</sub> (for one day), BOD<sub>5</sub> (for 5 days) or, finally, BOD<sub>20</sub> = BOD<sub>t</sub> (total). Usually the 5 day oxygen deficiency is determined (BOD<sub>5</sub>) and it is considered that complete decomposition of the organic matter in the water is achieved when the BOD<sub>5</sub> drops to 2 mg per litre, i.e. reaches a value typical of clean natural water. The addition of organic matter to water changes its composition and disrupts the normal regime of the basin, causes the water to “flower”, or in some cases brings about massive destruction of seaweeds and pollution of the water. The most dangerous for living matter are such toxic organic compounds as phenols, tars, mercaptans, hydrogen sulphide and some others. Their addition to water poisons it, makes it unfit for use as drinking water, communal uses, use by domestic animals.

Contamination of water basins results in great economic damage to many branches of the economy and there is a threat of a deficiency of pure drinking water. A deficiency of drinking water has become to be felt also because of the tremendous consumption of fresh water by industry. The most radical means for protecting water basins from depletion and contamination is to sharply reduce the discharge of industrial wastes to them, or better yet, to completely eliminate them by employing full recycle processes. Maximum economizing in water consumption in production processes can lead to reduced discharge of liquid wastes; their complete elimination accompanied by minimum consumptions of fresh water can only be achieved by using no-effluent closed-cycle processes. Results obtained in designing such processes have proved that besides their other positive features, closed-cycle water supply processes are more economical than open cycle ones with a liquid wastes purification system.

At the present time recycle systems with reuse of aqueous effluents of several types are employed on a wide scale in industry: (a) return

of the purified wastes to the same process; (b) utilization of the liquid effluent from one stage of the process in a following stage; (c) utilization of the purified wastes in diverse technological processes or for satisfying other needs. There are other possible ways of limiting the volume or completely eliminating wastes discharges: complete evaporation, pumping extremely polluted liquid wastes into geologically isolated strata, controlling the discharge to water basins by means of special reservoirs (accumulators) which simultaneously serve for purification. The second basic method for protecting water basins is to develop reliable ways for liquid wastes purification. A great deal of effort is being devoted in the USSR to construction of purification units and to developing new methods for purifying liquid wastes. The method employed depends on the volume of the discharges and on the content, size dispersion and composition of the impurities. Since, as a rule, there is a variety of impurities and they are of a complex nature, usually a number of different purification methods are used.

According to the basic principle of purification the methods used for decontaminating liquid wastes can be divided into the following groups: (1) mechanical; (2) physicochemical; (3) chemical; (4) biochemical; and (5) thermal.

**Mechanical methods** include settling, filtering and clarification operations. This method is the easiest to realize and is used for separating large-size suspended particles, usually as the first stage of the overall purification flow scheme. The equipment employed is standard equipment for mechanical liquid purification: settling basins, sieves, filters, etc.

**Physicochemical methods** used for purifying waste waters include flotation of fine-particle suspensions, their coagulation using flocculants and coagulating agents, adsorption of dissolved matter (on activated carbon, ash, slag), extraction with solvents, removal by distillation with steam, by ion exchange, etc. Flotation of fine-particle suspensions and their coagulation are most often classified as mechanical methods, although they are based on processes of a physicochemical nature (see Part I, Chapter 7). These operations, and also filtration, are carried out directly after the separation of large-size particles by the techniques of primary mechanical purification.

The use of expensive reagents and of quite complex apparatus are necessary for physicochemical purification. These techniques can expediently be employed mainly in purifying multicomponent waste waters containing only small amounts of toxic matter. Adsorption on activated carbon or ion exchange is used for removing copper, zinc, nickel and lead from the wastes of non-ferrous-metallurgy plants. Ion exchange on a cationite filter is employed for this (see Part I, Fig. 131). Phenols are separated from waste waters by extraction with petroleum-base oils, benzene or carbon tetra-

chloride, and also by distillation with steam and passing the steam through a NaOH solution to regenerate the component of value in it as a sodium phenolate.

**Chemical methods** are based on treating the waste waters with chemicals to form non-toxic products by reactions of neutralization, condensation, oxidation or reduction. These methods require the expenditure of large amounts of reagents and result in the formation of new compounds, which although they are not by themselves toxic, foul-up rivers and lakes. To this group belong such processes as chlorination—treating effluent streams with chlorine or its oxygen compounds. This technique is often employed for decontaminating waste, its deodorization, destroying fungi and other harmful matter in it, converting cyanide compounds to a harmless form, etc.

The most promising and reliable of the methods of waste purification are the biochemical and thermal ones.

**Biochemical purification** is employed mainly for wastes which contain organic matter either as an independent method or in combination with another one. Biochemical purification consists in destroying organic and some inorganic pollutants using a microorganism culture of a specific nature. By means of oxidizing biochemical reactions, organic compounds (and also inorganic sulphides and ammonium salts) can be converted into harmless oxidation products: water, carbon dioxide, nitrate and sulphate ions, etc. Making use of bacteria most organic impurities can be almost completely oxidized when present in industrial waste waters at low concentrations. The MPL of matter to be subjected to biochemical purification (in g/m<sup>3</sup>) are: for organic acids (butyric, acrylic) 100-500; alcohols and ethers 300-500; ions of metals (Zn, Ni, Cr) 1-10; phenol 1000. A drawback of biochemical purification is the low rate of the oxidation process and, as a result, the large volume of the apparatus needed to carry it out to completion.

Two different techniques are used in biochemical purification: one with oxygen present (aerobic), the other in the absence of oxygen (anaerobic). The aerobic technique is more universal and is used more extensively; it provides a higher processing rate and gives maximum destruction and decontamination of the pollutants. The anaerobic technique is employed in the primary stage of biochemical purification of wastes with a high content of organic matter. A 10- to 20-fold decrease in the concentration in the first stage creates favourable conditions for the following aerobic purification.

Biochemical purification of industrial (and also municipal sewage) waste is carried out at filtration fields (specially prepared land areas), in biological purification ponds (a cascade of man-made basins), biofilters and aerotanks. The most extensively used and the most promising for future developments are biofilters and aerotanks. Biofilters (Fig. 118) are perforated-floor reinforced-concrete reser-



voirs filled with a packing which contain microorganisms forming a so-called biological film on the surface of the packing elements. The waste enters the apparatus through a dispersing device (a rotating sprayer, for example) which provides uniform distribution over the packing, then filters down through the packing in contact with the biofilm on its surface. Air is either forced up through the perforated floor by a blower or natural ventilation is employed, which is more economical. Forced ventilation is used when the height of the packing exceeds 2 m, or when it is necessary to desorb large amounts of  $\text{CO}_2$ . Porous, high-strength materials, such as slag,

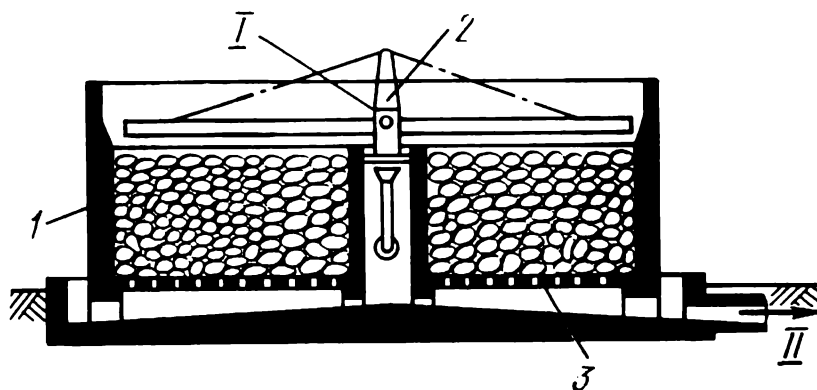


Fig. 118. Schematic diagram of a biological filter with a rotary sprayer:  
1—packing; 2—rotary sprayer; 3—perforated bottom. I—contaminated waste-water feed to purification unit; II—purified water exit

crushed rock, gravel, coke, ceramsite, or plastic blocks are employed as the packing. Biofilters are of a circular shape with diameters from 6 to 30 m and corresponding capacities of 1000 to 40 000 cu m per day purified water. The purification efficiency of a biofilter depends on the BOD load\*, the packing height, packing-element size, uniformity of distribution of the waste water and air across the packing, etc. Usually the BOD remainder in the effluent is 10-25 g/m<sup>3</sup> (for initial BOD values of 150-1500 g/m<sup>3</sup>). Fig. 119 is a schematic diagram of a biofilter unit with changeable directions of recirculation of the waste water. Recirculation is necessary to wash the used-up film (decomposition products) from the surface of the filter packing.

Most convenient in operation, more easily controlled apparatus for biochemical clean-up are aerotanks. Aeration basins are reinforced-concrete reservoirs (30-100 m long, 3-10 m wide and 3-5 m high) into which air is continuously and uniformly supplied. They are equipped with one of a number of devices for dispersing the air—perforated plates, perforated tubes, nozzles, aerators with removable diffusers made of a porous plastic, etc. The two phases are sometimes mixed mechanically using stirrers and also by providing different

\* The BOD load is expressed in g/m<sup>3</sup> per cubic metre of biofilter volume.

directions of movement to the liquid and introducing it at various points. The biochemical oxidation in the aerotank is caused by "activated sludge", i.e. by aerobic bacteria gathered into flakes which form when the bacteria culture is mixed with the waste water. The activated sludge is distributed throughout the apparatus as

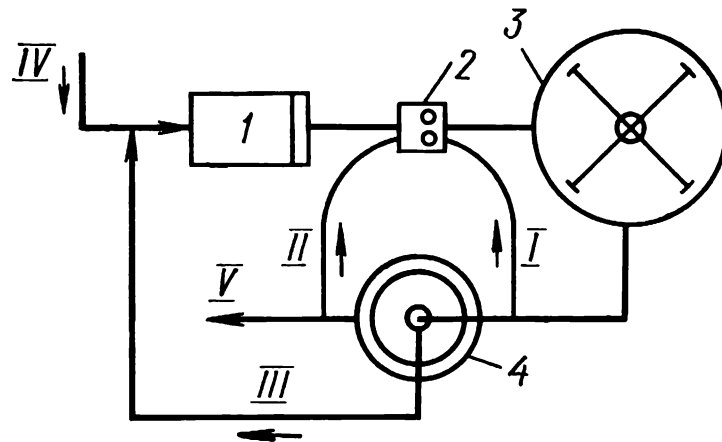


Fig. 119. Flow diagram of a biological filter unit with recirculation of the waste water:

1—primary settling basin; 2—pumps; 3—biological filter; 4—secondary settling basin. I, II, III—recirculation of the waste water; IV—waste water, to purification; V—purified waste water

a suspension. Intensive aeration of the waste water creates favourable conditions for growth of the bacteria to form sludge flakes on which dissolved and colloid impurities adsorb and decompose. Biochemical-purification units usually consist of a number of inter-

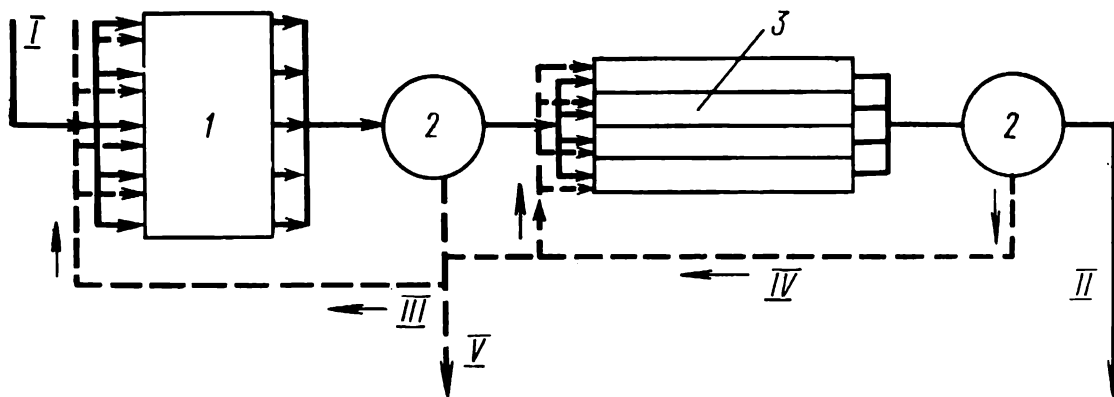


Fig. 120. Flow diagram of a two-stage unit for purifying water in aerotanks:

1—aerotank mixer; 2—settling basin; 3—aerotank reactors. I—waste water, to purification; II—purified water; III—activated sludge, 1<sup>st</sup> stage; IV—activated sludge, 2<sup>nd</sup> stage; V—excess activated sludge

connected aerotanks plus mixers, settling basins and other apparatus necessary for purifying the water, recycling it and regenerating the activated sludge.

A flow diagram of a modern two-stage unit for purifying waste water in aerotanks is shown in Fig. 120. Units of this type have

waste-water capacities of tens to hundreds of cubic meters per day and provide high BOD removal efficiency. For example, in two-stage aerotanks purification of the waste water of synthetic alcohols production the BOD is lowered from 800 to 15 g/m<sup>3</sup>, of producing phenol and acetone—from 1100 to 10 g/m<sup>3</sup>, synthetic rubber—from 430 to 20 g/m<sup>3</sup>, and from petroleum refineries—from 800 to 20 g/m<sup>3</sup>.

The thermal method of decontaminating waste water consists, essentially, in the complete oxidation (combustion) at high temperatures of toxic pollutants to produce non-toxic gaseous combustion

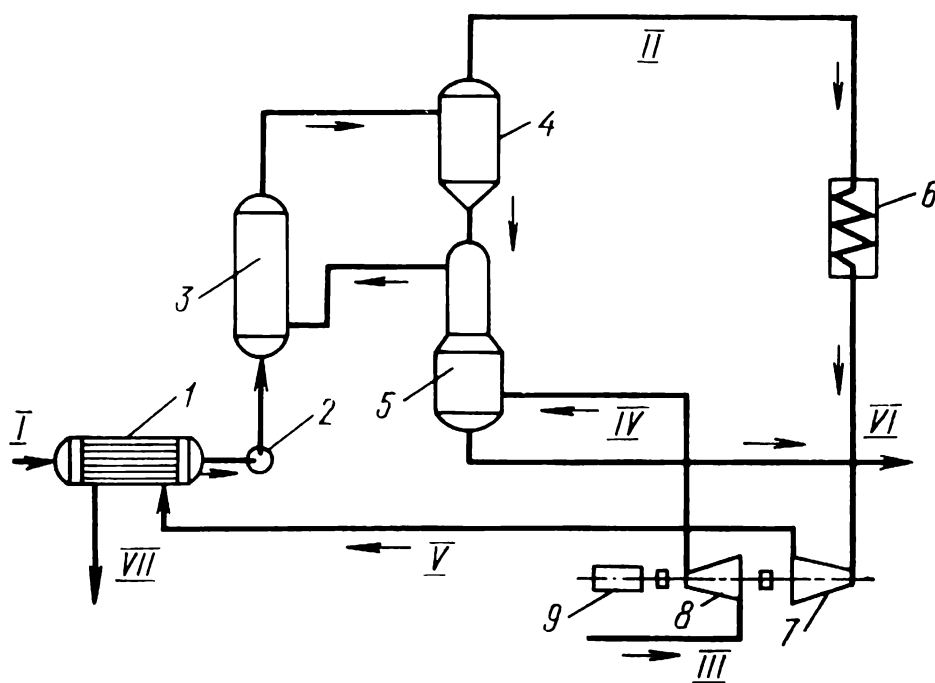


Fig. 121. Flow diagram of a unit for wet oxidation of sulphite waste liquor:

1—heat exchanger; 2—pump; 3—wet-oxidation reactor; 4—separator; 5—thickener; 6—superheater; 7—turbine; 8—compressor; 9—generator. I—sulphite waste liquor; II—gas-vapour mixture; III—air; IV—compressed air; V—stack gas; VI—liquid effluent containing no organic impurities; VII—condensate

products and a solid remainder. In the process huge amounts of water must be evaporated and this requires the expenditure of large amounts of fuel, steam or electric power and the apparatus used must be very large. A positive feature of the method is its universality, i.e. it completely destroys harmful pollutants regardless of their nature. The thermal method is especially suited for use with waste water containing large amounts of nonvolatile organic matter, for example the spent liquor of pulp production by a sulphite process, which contains 6-8% organic matter. In such units the waste serves as a "fuel", and a positive economic effect is achieved by burning it; for example, steam is produced. A wet-combustion unit consists of standard unit apparatus—furnaces of one of a number of types, autoclaves, heat exchangers, separators, cyclones, etc.

Fig. 121 is a flow diagram of a unit for wet combustion of the spent liquor of pulp production by a sulphite method. The hot

spent liquor is heated further, to 150°, in a heat exchanger by the excess heat of the effluent gas and pumped into an autoclave-like reactor. In the reactor at 270-300° and 100 atm the organic matter of the spent liquor is completely oxidized to water and CO<sub>2</sub>. The gas-liquid mixture is divided in a separator. The effluent water, which contains no organic impurities, is passed through a heat exchanger (not shown in the flow diagram) and is then either discharged or reused. The high-pressure gas steam mixture, after being passed through a superheater, is utilized in power turbines, compressors and other machines of the paper-and-pulp process; the spent steam is also utilized. At present sulphite spent liquor is usually processed to produce alcohol and other products, the waste liquor being subjected to biochemical purification.

Table 24 lists comparative data on the different methods used for purifying liquid wastes.

TABLE 24

The Efficiency of Various Waste-Purification Methods

Purification method	Purification, %			Operating costs of equipment for purifying 1 m <sup>3</sup> water, kop.
	suspensions	dissolved matter	BOD	
Mechanical	60-80	—	30-40	—
Physicochemical:				
coagulation and flotation	80-85	—	40-50	—
ion-exchange adsorption	90	—	50-75	20-25
stripping with steam	—	90-93*	—	—
Biochemical:				
in biofilters	90	—	80-90	4-6
in aerotanks	90	—	90-97	4-6

\* In removing phenols

The comparison is clearly in favour of biochemical purification, especially for use as the final stage of water purification. Table 24 does not contain data on the thermal method which does away completely with waste discharge. This method is as yet not economically feasible, especially when the volume of waste is large. Moreover, the possibility of its employment depends on the composition of the effluent.

### 5. An Example of Design Calculations for an Aerotank Reactor for Cleaning Effluents

In order to determine the size of the aerotank, the aeration time and the consumption of compressed air one must know the degree of purification to be achieved and choose the purification method and type of equipment to use. To calculate the volume of the aerotank, data must be available concerning the rate of the biochemical processes and also the rates of heat and mass transfer. The order in which the calculations should be carried out can be represented as follows:

(1) obtaining the data on which the calculations are to be based—the volume of effluent liquid, pollutants concentration, variations in effluent flow-rate; (2) determining the necessary degree of purification; (3) selection of purification method and type of purification equipment; (4) calculating the basic dimensions of the aerotank and other apparatus for the given conditions.

The basic data for the calculations, i.e. the volume of process waste, its pollutant content, flow-rate variations, are usually known. The purification degree is now determined. Its value must correspond to sanitation regulations governing discharge of waste to rivers and lakes.

The general expression describing the relationship between the required degree of purification and the sanitation regulations level is given by

$$C_d L_d + C_{upst} L \cdot a \leq (aL + L_d) \cdot C_{MPL} \quad (11.16)$$

$C_d$  being the permissible concentration of a pollutant at which level, according to regulations, the liquid can be discharged to a stream or lake, g per m<sup>3</sup>;  $C_{upst}$ —the concentration of the pollutant upstream of the effluent discharge point; g per m<sup>3</sup>;  $C_{MPL}$ —the maximum permissible concentration of the pollutant in the water of the stream, g per m<sup>3</sup>;  $L$ —stream volumetric flow rate in “dry” months, m<sup>3</sup> per sec;  $L_d$ —assumed volumetric flow of process waste discharge, m<sup>3</sup> per sec;  $a$ —a mixing factor, which gives the fraction of the overall stream flow  $L$  that mixes with the discharge. The mixing factor value is calculated as

$$a = \frac{1 - e^{-\alpha \sqrt[3]{l}}}{1 + e^{-\alpha \sqrt[3]{l}}} \quad (11.17)$$

where  $l$  is the distance downstream between the discharge point and the site for which the calculations are being made measured along the main stream path, m, and  $\alpha$  is a constant which accounts for the hydrodynamic mixing conditions,

$$\alpha = \varphi \xi \sqrt[3]{\frac{D_t}{L_d}} \quad (11.18)$$

$\xi$  being a river-meandering factor equal to the ratio of the distance from the discharge point to the measuring point along the main stream path with respect to the distance measured along the straight line connecting them;  $\xi$  is assumed equal to 1 for discharge at the shore and 1.5 for discharge in the main stream;  $D_t$  is the turbulent diffusivity value for plain land streams;

$$D_t = \frac{w_m H_m}{200} \quad (11.19)$$

where  $w_m$  is the mean flow rate in the part of the stream being considered, m per sec;  $H_m$ —the mean river depth, m.

Next,  $n$ , the dilution-factor value just upstream of the point where water is taken for use, is calculated

$$n = \frac{aL + L_d}{L_d} \quad (11.20)$$

The required degree of purification,  $x$ , can be found on the basis of the following data: (a) suspended matter, (b) sum BOD of the waste water and stream water ( $BOD_s$ ), (c) dissolved-oxygen content of the water, (d) maximum permissible sum level of pollutants, (e) stream temperature and (f) stream pH.

The maximum level of suspended matter permitted by sanitation regulations in an effluent discharged to a stream is given by the formula

$$m = C_{MPL} \left( \frac{aL}{L_d} + 1 \right) + C_{in} \quad (11.21)$$

$C_{MPL}$  being the maximum permissible level of suspended matter in the stream to which the effluent has been discharged, g per  $m^3$ ;  $C_{in}$  the initial content of suspended matter in the stream water, prior to addition of the waste, g per  $m^3$ . The required purification degree with respect to suspended matter is given by

$$x = \frac{C - m}{C} \cdot 100 \quad (11.22)$$

where  $C$  is the concentration of the process effluent before purification, g/ $m^3$ .

The concentration of pollutants in the waste expressed as BOD is given by

$$C'_d = \frac{aL}{L_d \cdot 10^{-k_d \tau}} (C'_{MPL} - C'_s \cdot 10^{-k_s \tau}) + \frac{C'_{MPL}}{10^{-k_s \tau}} \quad (11.23)$$

where  $C'_d$  is the  $BOD_s$  of the purified waste water effluent, g/ $m^3$ ;  $C'_s$ —the BOD of the stream water above the spot of discharge, g/ $m^3$ ;  $k_d$  and  $k_s$  are the oxygen consumption rate constants in the discharge and stream water (determined by analysis);  $\tau$  the time required

for the water to flow from the discharge spot to the spot for which the calculations are being made, days and  $C'_{\text{MPL}}$  is the maximum permissible  $\text{BOD}_s$  level of the mixture of stream water and waste,  $\text{g/m}^3$ . Usually  $C'_d = C'_s = C_1$  and the biological oxygen demand of the mixture of waste water and stream water is

$$C'_t = C'_a \cdot 10^{-C_1 \tau} \quad (11.24)$$

where  $C'_t$  is the permissible  $\text{BOD}_s$ -level and  $C'_a$ —the  $\text{BOD}_s$  of the waste-stream water mixture at the waste discharge,  $\text{g/m}^3$ . The dependency of the oxygen consumption rate constant on the temperature is described by  $k_{T^\circ} = k_{(20^\circ)} \cdot 1.047^{(T-20)}$ . The permissible  $\text{BOD}_s$  of waste discharged to the stream is

$$C'_d = \frac{a}{L_d} (C'_a - C'_s) + C'_a \quad (11.25)$$

The necessary degree of purification is

$$x = \frac{C'_{\text{in}} - C'_d}{C'_{\text{in}}} \cdot 100 \quad (11.26)$$

where  $C'_{\text{in}}$  is the initial  $\text{BOD}_s$  of the waste water, before purification,  $\text{g/m}^3$ .

Oxygen-regime calculations are carried out without taking into account natural mixing in the stream (reaeration). The amount of oxygen dissolved in the stream water must not be below  $4 \text{ g/m}^3$  (for basins in which fishing is economically important—not below  $6 \text{ g/m}^3$ ). The  $\text{BOD}_s$  of the waste discharged (after purification) for such a condition can be calculated using the formula

$$C'_d = \frac{aL}{L_d} (C_{\text{O}_2} - 0.4C'_s - 4) - \frac{4}{0.4} \quad (11.27)$$

where  $C_{\text{O}_2}$  is the dissolved oxygen in the stream water upstream from the discharge point,  $\text{g/m}^3$ ; 0.4—a factor for converting from  $\text{BOD}_s$  to  $\text{BOD}_2$ ; 4 is the minimum permissible level of oxygen in the stream water fixed by sanitation regulations,  $\text{g/m}^3$ . Following this the necessary degree of purification can be determined using (11.26).

The permissible concentration of the harmful substance in the waste water discharged to the stream can be found using the following formula

$$C_d = \frac{aL}{L_d} (C_{\text{MPL}} - C_{\text{act}}) + C_{\text{MPL}} \quad (11.28)$$

where  $C_{\text{MPL}}$  is the maximum permissible level of a pollutant, in the water,  $\text{g/m}^3$ ; and  $C_{\text{act}}$  is the actual concentration of the pollutant,  $\text{g/m}^3$ . The necessary degree of purification is found using an equation of type (11.26).

The maximum permissible level of acids and alkalis in effluent waste discharged to a stream is given by the equations

$$Ac = a (L/L_d) V_{ac} \quad (11.29)$$

$$Alk = a (L/L_d) V_{alk} \quad (11.30)$$

where  $V_{ac}$  and  $V_{alk}$  are the permissible volumes of acid and alkali which can be discharged into the stream, in terms of 1 N alkali or acid, ml;

$$V_{ac} = 0.5 \cdot C_{alk} - 0.01 \cdot C_{CO_2} \quad (11.31)$$

$$V_{alk} = 0.02 \cdot C_{CO_2} - 0.01 \cdot C_{alk} \quad (11.32)$$

$C_{alk}$  being the alkalinity of the stream water in terms of 1 *n* acid, ml;  $C_{CO_2}$ —the  $CO_2$  concentration of the stream water, ml

$$\log C_{CO_2} = 8.16 - pH + \log C_{alk} \quad (11.33)$$

The next necessary step is to check on whether the waste water must be cleaned with respect to its colour, taste or odour. When the degree of purification has been determined, the biochemical method to be used is chosen. The design calculations of all the aeration station structures—of a technological and hydrodynamics nature—are carried out as usual. Let us consider as an example the calculations for an aerotank for final purification, i.e. such that the water can be discharged to a stream. The volume of air for treating one cubic metre of waste water is found by applying the formula

$$V_{sp} = \frac{2 \cdot C'_{in}}{\alpha h} \quad (11.34)$$

where  $\alpha$  is an air utilization factor assumed equal to 12 g/m<sup>4</sup> for porous filter plates and 6 g/m<sup>4</sup> for perforated pipes;  $h$  is the operating depth of the aerotank and  $C'_{in}$  is the  $BOD_s$  of the waste water before purification, g/m<sup>3</sup>.

The period of aeration in the tank in hours is calculated using

$$\tau = \frac{2 \cdot C'_{in}}{\alpha I} \quad (11.35)$$

$I$  being the aeration intensity, m<sup>3</sup>/m<sup>2</sup> · hr, usually an  $I$ —value of 4.4 m<sup>3</sup>/m<sup>2</sup> · hr is selected. The necessary aeration period can also be calculated on the basis of the sanitation regulations. The volume of air  $V$  in m<sup>3</sup>/hr which must be fed to the aerotank is calculated from

$$V = V_{sp} \cdot L_d \quad (11.36)$$

The horizontal cross-section area  $F$ (m<sup>2</sup>) of the aerotank and the corridor length (aerotank sections)  $l$  (m), are found, from

$$F = \frac{V}{I} \quad (11.37)$$



The aerotank volume  $V_{\text{aero}}$ ,  $\text{m}^3$ , is

$$V_{\text{aero}} = Fh \quad (11.38)$$

and the corridor length is determined as  $l = F/b$ , where  $b$ , the width of the corridors, lies between  $h$  and  $2h$  m. The rate of activated sludge circulation  $m_{\text{sl}}$  is selected at 30-70% of the average waste liquid flow rate, or is calculated using the following equation

$$m_{\text{sl}} = \frac{C_{\text{sl.mix}} - C_{\text{susp}}}{C_{\text{sl}} - C_{\text{sl.mix}}} \cdot 100 \quad (11.39)$$

where  $C_{\text{sl.mix}}$  ( $C_{\text{sl.mix}} = 2000\text{-}3000$  mg/l) is the concentration of the activated sludge in the sludge mixture supplied to the secondary sedimentation tank (see Fig. 119);  $C_{\text{susp}}$ —the concentration of suspended matter in the liquid entering the aerotank, mg/l;  $C_{\text{sl}}$ —the concentration of recycled sludge (5000-6000 mg/l). The flow rate of the sludge  $L_{\text{sl}}$  ( $\text{m}^3/\text{sec}$ ) is

$$L_{\text{sl}} = \frac{m_{\text{sl}}}{100} \cdot L_{\text{D}} \quad (11.40)$$

Accumulated, excess sludge must be regularly discharged.

From this short discussion of purification of gaseous effluents and industrial waste it follows that methods now in use for cleaning-up industrial discharges to the environment require very big expenditures (both—capital investments and expenditures to cover operational costs), large-sized structures and complicated, multistage purification systems. Moreover purification units now in use often do not meet sanitation-regulations standards on the remainder levels of toxic ingredients of gaseous and liquid discharges. This is especially true for waste-liquid purification, for which the purification units usually do not provide complete protection against contamination of streams and lakes.

Protection of the atmosphere and of streams and lakes from contamination will in the future be assured by a sharp decrease, and eventually complete cessation, of industrial waste discharge by creating low discharge or no-discharge production processes. For this new technological processes must be developed which lead to a change-over from production methods with discharge to the environment to methods which completely eliminate them. Experience gained in designing no-discharge processes shows that they not only provide environmental protection but also result in large product-cost reductions.

The general direction in developing no-discharge plants not harmful to the environment, is toward the use of cyclic flow schemes of individual production processes and a closed cycle scheme for the overall production process. Another simultaneous tendency is to achieve complete, integral utilization of all the components in the raw materials and set-up integrated combinations of plants. There

is a gradual movement in industry toward no-discharge processes. An example is the growth in the USSR in the share of soda-ash produced by integral processing of nephelines, without waste and discharge, in place of the ammonia process which produces large amounts of polluted waste. A sharp reduction of industrial environmental contamination can be achieved by improving existing technological processes, maintaining optimal process parameters, which provide maximum yield of valuable products. Together with progress in setting-up no-discharge, not harmful production processes there must be progress in the field of gas- and liquid-waste purification and purification methods used must be continuously improved.

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